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A degradation model for solid oxide fuel cell anodes due to impurities in coal syngas

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A DEGRADATION MODEL FOR SOLID OXIDE FUEL CELL ANODES DUE TO IMPURITIES IN COAL SYNGAS

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Dissertation submitted to the
College of Engineering and Mineral Resources
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Doctor of Philosophy
in
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Surface Reactions, Multi-Component Diffusion
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ABSTRACT

A DEGRADATION MODEL FOR SOLID OXIDE FUEL CELL ANODES DUE TO IMPURITIES IN COAL SYNGAS

Fatma Nihan Cayan

Solid Oxide Fuel Cells (SOFCs) offer great promise as a clean and efficient alternative to conventional power generation technologies. A major advantage of SOFCs in comparison to other fuel cell types is that they can be operated directly on a wide variety of fuels including biogas, hydrocarbon fuels and coal-derived synthesis gas (syngas). SOFC operating on coal syngas is an especially attractive prospect given the abundant coal resources in the world. However, coal syngas usually contains various impurities such as phosphorus, arsenic, zinc, sulfur, mercury, selenium, and vanadium which affect the performance and durability of SOFCs. At low impurity concentrations, degradation rates are quite slow and long term experiments (more than 1000 h) are required in order to determine the cell degradation rates accurately. Theoretical models that can predict the degradation behavior of SOFCs operating on syngas with very low levels of impurities could substantially reduce the time and effort involved in durability experiments.

In an attempt to predict the typical degradation patterns observed in Solid Oxide Fuel Cell (SOFC) anodes due to coal syngas contaminants such as arsenic (As) and phosphorous (P), a new phenomenological model is formulated. The model includes gas phase diffusion including Knudsen diffusion and surface diffusion within the anode and the adsorption reactions on the surface of the Ni-YSZ based anode. Model parameters such as reaction rate constants for the adsorption reactions are obtained through indirect calibration to match the degradation rates reported in the literature for arsine (AsH_3), phosphine (PH_3), hydrogen sulfide (H_2S) and hydrogen selenide (H_2Se) under accelerated testing conditions. Current simulation results from implementation of the model demonstrated that the deposition of the impurity on the Ni catalyst starts near the fuel channel/anode interface and slowly moves toward the active anode/electrolyte interface which is in good agreement with the experimental data. Parametric studies performed at different impurity concentrations and operating temperatures showed that the coverage rate increases with increasing temperature and impurity concentration, as expected.

The calibrated model was then used for prediction of the performance curves at different impurity concentrations and operating temperatures. Encouraging agreement was obtained between the predicted results and the experimental data reported in the literature. Synergistic effect of various impurities including AsH_3 , PH_3 and H_2S was also

examined and it was concluded that the mixture of impurities leads to faster degradation and thus shorter lifetime of the cell when compared to that of a single impurity.

To my only sunshine

Canım Oğlum'a

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NOMENCLATURE

As	arsenic
a_s	specific catalyst area, m^{-1}
Be	beryllium
c	diffusivity model parameter
Cd	cadmium
Cl	chlorine
Cr	chromium
D_θ	transport coefficient, $\text{m}^2 \text{s}^{-1}$
D_i^k	Knudsen diffusivity, $\text{m}^2 \text{s}^{-1}$
D_{ij}	binary diffusivity, $\text{m}^2 \text{s}^{-1}$
D_i^{k*}	effective Knudsen diffusivity, $\text{m}^2 \text{s}^{-1}$
D_{ij}^*	effective binary diffusivity, $\text{m}^2 \text{s}^{-1}$
$E_{act,i}$	activation energy barrier, J mole^{-1}
E_N	Nernst potential, V
F	Faraday's constant, C mole^{-1}
G	Gibbs function, J mole^{-1}
Hg	mercury
i	total current density, A m^{-2}
i_{ref}	reference current density, A m^{-2}
i_o	exchange current density, A m^{-2}
K	potassium
k_r^+	forward reaction rate constant for methane steam reforming reaction, $\text{mol m}^{-3} \text{s}^{-1} \text{Pa}^{-2}$
k_r^-	backward reaction rate constant for methane steam reforming reaction, $\text{mol m}^{-3} \text{s}^{-1} \text{Pa}^{-4}$
k_s^+, k_s^-	forward and backward reaction rate constants for water gas shift reaction, $\text{mol m}^{-3} \text{s}^{-1} \text{Pa}^{-2}$

$k_{f,H}, k_{b,H}$	forward and backward reaction rate constants for hydrogen adsorption, s^{-1}
$k_{f,X}, k_{b,X}$	forward and backward reaction rate constants for contaminant X adsorption, s^{-1}
k_m	mass transfer coefficient, $m\ s^{-1}$
M_i	molecular weight of , $g\ mole^{-1}$
M_{avg}	average molecular weight, $g\ mole^{-1}$
m	degradation model parameter
n	diffusivity model parameter
n	degradation model parameter
$\mathbf{n}$	vector of mole fractions
N_i	molar flux, $mole\ m^{-2}\ s^{-1}$
$\mathbf{N}$	stoichiometric matrix
Na	sodium
P	pressure of the system, Pa
P	phosphorous
P	power density, $Watt\ m^{-2}$
P^*	modified power density
Pb	lead
p	degradation model parameter
q	degradation model parameter
R_u	universal gas constant, $J\ mol^{-1}\ K^{-1}$
R_i	molar production rate of species i due to homogenous reactions, $mole\ m^{-3}\ s^{-1}$
$\langle r \rangle$	mean pore diameter, μm
Sb	antimony
Se	selenium
Sh	Sherwood number
S_i	net production rate of species i due to surface reactions, $mole\ m^{-3}\ s^{-1}$

T	temperature of the system, K
t	time, s
V	vanadium
X, Y	Typical contaminant
y_i	mole fractions
Zn	zinc

Greek

α	transfer coefficient
δ	anode thickness, m
ε	porosity
ε_0	porosity at zero percent contaminant coverage
ϕ	electrical potential, V
η_i	overpotentials, V
Γ	site density, mol m ⁻²
μ	vector of species chemical potentials
Π	Thiele modulus
θ_i	surface coverages
σ	electrical conductivity, S m ⁻¹
σ_0	electrical conductivity at zero percent contaminant coverage, S m ⁻¹
τ	tortuosity
ν_i	stoichiometric coefficient
ω_{θ_i}	source terms due to surface adsorption reactions
ξ	extent of reaction

CHAPTER 1- INTRODUCTION

1.1 Background

Modern lifestyles have resulted in increasing levels of energy consumption. To supply the demand for the ever increasing levels of the energy, traditional power generation techniques including combustion of fossil fuels have been widely used over the last century. Coal is the most abundant, readily available and economical fossil fuel in the world. At current production levels, proven coal reserves are estimated to last approximately 225 years [1]. However, an undesirable consequence of coal combustion is environmental contamination, as a result of the combustion by-products released to the atmosphere. Moreover, coal combustion is not an efficient way to generate electrical power, since burning coal to produce steam for electrical power production is limited by the Carnot Cycle Efficiency.

Fuel cells appear to be an attractive alternative to traditional power generation methods. A fuel cell is a device that generates electricity by combining a fuel and an oxidant electrochemically, rather than thermochemically, as is the case with the conventional fossil fuel combustion. Electrochemical power generation has many advantages over fossil fuel combustion, including higher efficiency, low pollution and low equipment maintenance. The fuel cell receives the reactants that take place in the energy conversion process in a continuous manner, unlike batteries, which use chemical energy that is stored within the electrodes. Since the first demonstration of the fuel cell principle by Sir William Grove in 1839 [2], many types of fuel cells, namely Alkaline Fuel Cell, Proton

Exchange Membrane (PEM) Fuel Cell, Direct Methanol (DM) Fuel Cell, Phosphoric Acid (PA) Fuel Cell, Molten Carbonate (MC) Fuel Cell, Solid Oxide Fuel Cell (SOFC) have been developed. Figure 1.1 shows the summary of the most common fuel cell types.

Figure 1. 1: Common Fuel Cell types

Among them, Solid Oxide Fuel Cells (SOFCs) have become one of the most viable candidates for future power plants due to their high efficiency and fuel flexibility.

1.2 The Solid Oxide Fuel Cell (SOFC)

The SOFC is a high temperature fuel cell that has many advantages as an energy conversion device, especially for stationary applications. The main components of a fuel cell are the electrolyte and the electrodes. The electrolyte of an SOFC is an ionically conducting ceramic membrane that prevents direct combination of the fuel and the oxidant. This membrane is sandwiched between two porous, electronically (or mixed) conducting electrodes: the anode on the fuel side and the cathode on the air side.

The electrolyte is a dense, gas-tight ceramic layer, traditionally made of yttria-stabilized zirconia (YSZ), which is a good conductor of oxide ions, O^{2-} . An electronically conductive, gas tight interconnect plate provides the series connection of unit cells constituting an SOFC stack.

Since ionic conductivity in ceramics is a thermally activated process, high operating temperatures are required to obtain sufficient overall conductivity in the fuel cell. YSZ exhibits acceptable conductivity above 600° C. The oxide ion, O^{2-} , allows the use of a variety of fuels other than hydrogen, such as carbon monoxide or any hydrocarbon fuel, either by direct oxidation or through steam reforming. Another important feature of the high operating temperature is the possibility to use the exhaust heat in a power generating bottoming cycle, using either a gas or steam turbine. These features give the SOFC great versatility compared to other fuel cell types, as well as creating the possibility of generating electrical power at very high efficiencies. On the other hand, the elevated operation temperature requires long start-up periods.

The porous anode made of a composite nickel/yttria-stabilized zirconia (Ni/YSZ) is catalytically active for the oxidation reaction and retains sufficient ionic as well as electronic conductivities. Similarly, the porous cathode made of lanthanum manganite ($LaMnO_3$) doped with strontium (Sr), LSM, is able to catalyze dissociation of oxygen and has good electronic conductivity in the presence of air. There are three basic designs of the SOFCs are available: cathode-, electrolyte- and anode-supported.

For electricity generation in SOFCs, oxygen molecules in the cathode pores dissociate at the surface of the catalyst (e.g. LSM) and combine with free electrons coming from the external circuit, and the resulting oxide ions move through the electrolyte toward the anode. In the anode, the oxide ions combine with hydrogen, carbon monoxide or hydrocarbon molecules to form H_2O and CO_2 . The electrons released in the oxidation reaction have to escape through an external circuit, creating usable electricity and closing the loop. Figure 1.2 depicts schematically the case of hydrogen and carbon monoxide being used as a fuel in an SOFC.

Figure 1. 2: Operation of solid oxide fuel cell

A unit cell generates approximately 1 V at open circuit conditions, with exact voltage depending on temperature, oxygen partial pressure, and reactant and product concentrations. This value is commonly known as open circuit voltage, or OCV. While operating, the delivered voltage is smaller than the OCV due to irreversible losses or cell

polarization. Polarization has been classified as activation, ohmic and concentration [3]. The activation polarization arises due to slow rate of electrochemical reactions. The ohmic polarization is a result of electrical resistance in the cell including ionic resistance to the flow of ions in the electrolyte and electronic resistance to the flow of electrons in the rest of the cell components. The concentration polarization is a resistance due to the mass transfer limitations in supplying reactants to the electrochemical reaction sites.

1.3 Utilization of Coal Syngas in SOFCs

Coal syngas is produced via a process called coal gasification in which coal is mixed with an oxidant (O_2 or air) and steam in a reactor operating under the pressure of 24-70 atm at 500~1800 °C to produce syngas containing carbon monoxide (CO), hydrogen (H_2), carbon dioxide (CO_2), water vapor (H_2O), methane (CH_4) and nitrogen (N_2) and also trace amounts of nearly all of the naturally occurring elements depending on the rank and geographical origin of the coal [4, 5]. Oxygen blown gasification is often used since less combustion of coal is needed to heat the reactants and less work is needed to compress the gases entering the reactor [5]. Moreover, oxygen blown gasification will help enable future CO_2 sequestration techniques [6]. Three types of coal gasification systems have been used throughout industry; namely, moving bed, fluid bed, and entrained flow. Table 1.1 shows the compositions of the raw syngas derived from these three major gasification systems [7]. The product syngas composition is extremely dependent on the coal as well as the gasification process. Table 1.2 shows trace impurities and their concentrations in the coal syngas generated by the gasification stream of Eastman Chemical Company's complex at Kingsport Tennessee and an estimate from University of North Dakota Energy and Environmental Research Center [8].

The combination of a coal gasifier with a SOFC not only provides clean energy by reducing the emissions but also may help reduce plant costs because high efficiency electrochemical systems should result in smaller physical plant size for a given electric power output as compared to conventional electricity generation techniques. Although recent studies have shown the feasibility of fueling SOFC systems with coal syngas [9-

11], the performance and the durability of SOFCs are affected by the presence of the impurity species in coal syngas. When a Ni-YSZ anode is operated in the impurity-containing syngas, the impurities may affect

- the mass transport of fuel gas molecules due to adsorption of the impurities on the anode surface forming secondary phases with the anode material to cause morphological changes via grain coarsening and consequent blockage of gas diffusion channels,
- the catalytic ability of Ni toward chemical and electrochemical reactions since impurity atoms on the surface poison (deactivate) triple phase boundaries,
- the ability of YSZ to transport the oxygen ions by forming other phases (zirconium silicate or phosphate are theoretically possible),
- the electrical conductivity of Ni by forming Ni alloys,
- the conductivity of interconnect-anode interface, and,
- the structural integrity of the Ni-YSZ anode and seal materials

The above material interactions may also affect other material properties, such as thermal conductivity, porosity and modulus of elasticity which, in turn, may lead to performance degradation. The effect of trace impurity species on the performance of SOFC anodes must be measured in order to (i) determine the required level for removal of these species from coal syngas before reaching the anode and (ii) to develop new anode materials that resist the attack of these undesired poisoning effects. Although it is possible to produce ultra-clean syngas by cleanup techniques, the cost of reducing the concentration of all potentially harmful impurities to sub-ppm levels will be very high.

The impact of major impurities, such as sulfur and carbon on the Ni-YSZ anode has been studied by researchers and the results are available in the literature [12-14]. However, the short term and long term effects of trace impurities like arsenic, phosphorus, selenium, chlorine and antimony on the SOFC performance are still unclear.

Table 1. 1: Syngas compositions generated by different gasifiers (vol %) [7]

Gasifier Type	Moving-Bed	Fluidized Bed	Entrained-Bed				
Manufacturer	Lurgi	Winkler	Destec	Koppers-Totzek	Texaco	Shell	Siemens
Coal	Illinois No.6	Texas Lignite	Appalachian Bit.	Illinois No.6	Illinois No.6	Illinois No.6	
Mole Percent							
Ar	trace	0.7	0.8	0.9	0.9	1.1	
CH ₄	3.3	4.6	0.6	-	0.1	-	0.002
C ₂ H ₄	0.1	-	-	-	-	-	-
C ₂ H ₆	0.2	-	-	-	-	-	-
CO	5.8	33.1	45.2	43.8	39.6	63.1	27.001
CO ₂	11.8	15.5	8.0	4.6	10.8	1.5	1.770
COS	trace	-	-	0.1	-	0.1	0.037
H ₂	16.1	28.3	33.9	21.1	30.3	26.7	13.211
H ₂ O	61.8	16.8	9.8	27.5	16.5	2.0	53.165
H ₂ S	0.5	0.2	0.9	1.1	1.0	1.3	0.421
N ₂	0.1	0.6	0.6	0.9	0.7	4.1	4.375
NH ₃ +HCN	0.3	0.1	0.2	-	-	-	0.006

Table 1. 2: Trace impurities and their concentration in coal syngas [8]

Contaminant	Concentration at the Kingsport Facility (ppmv)	UND-EERC Estimate
Arsine (AsH ₃)	0.15 to 0.58	0.2
Thiophene		1.6
Chlorine (Cl)		120
Methyl Fluoride (CH ₃ F)	2.6	
Methyl Chloride (CH ₃ Cl)	2.01	
Hydrogen Chloride (HCl)	<1	
Fe(CO) ₅	0.05 to 5.6	
Ni(CO) ₅	0.001 to 0.025	
CH ₃ SCN	2.1	
Phosphine (PH ₃)	1.9	
Antimony (Sb)	0.025	0.07
Cadmium (Cd)		0.01
Chromium (Cr)	<0.025	6.0
Mercury (Hg)	<0.025	0.002
Selenium (Se)	<0.15	0.17
Vanadium (V)	<0.025	
Lead (Pb)		0.26
Zinc (Zn)	9.0	

CHAPTER 2 - LITERATURE REVIEW

2.1 Effects of Coal Syngas Impurities on SOFCs

Given the fact that coal is the most abundant and readily available fossil fuel in the world, it will continue to play a significant role as an energy source for many years to come. With the rising concern about the effect of coal combustion by-products, such as greenhouse gases, on the environment, many countries are pursuing efforts to develop more sustainable energy systems to replace conventional boilers. Solid Oxide Fuel Cells (SOFCs) offer great promise as a clean and efficient alternative [15]. A major advantage of the SOFCs in comparison to other fuel cell types is that it can be operated directly on a wide variety of fuels including H_2 , biogas, hydrocarbon fuels and coal-derived synthesis gas (syngas) [15]. Although recent studies have shown the feasibility of fueling SOFC systems with coal syngas [9-11], the performance and the durability of SOFCs are affected by the presence of the certain impurity species such as phosphorus (P), arsenic (As), zinc (Zn), sulfur (S), mercury (Hg), selenium (Se), and vanadium (V), commonly found in the fuel stream which are found to react with the SOFC anode materials. It is difficult to completely remove these impurities and the clean-up processing is very expensive. Therefore, it is imperative that fuel cells be tolerant to these impurities up to a certain level.

Bao *et al.* [16] investigated the effect of several impurities including As_2 , HPO_2 , Cd, CH_3Cl , HCl, Hg, SbO and Zn in a simulated coal-derived syngas on SOFC performance at the temperatures ranging from 750°C to 850°C. Impurities were tested at relatively high concentration levels and short exposure duration, i.e., accelerated testing conditions. Of the contaminants tested, arsenic and phosphorus species degraded the performance rapidly. Both of these species resulted in a severe decrease in the observed cell power density with time of exposure. The As vapor species reacted with the Ni current collector in the anode to form nickel arsenides such as Ni_5As_2 causing electrical connectivity problems and eventually, cell failure. The phosphorus-species reacted with Ni to form nickel phosphides such as Ni_3P and also reacted with YSZ to form zirconium phosphates. The presence of CH_3Cl and Cd in fuel stream resulted in performance loss at temperatures above 800°C and significant power density loss was observed with 5 ppm Cd at 850°C. In order to determine the synergistic effects of presence of multiple contaminants in the fuel stream, Bao *et al.* [17] also performed tests with coal syngas containing mixtures of $\text{H}_2\text{S} + \text{AsH}_3$, $\text{H}_2\text{S} + \text{PH}_3$, or $\text{H}_2\text{S} + \text{AsH}_3 + \text{PH}_3 + \text{CH}_3\text{Cl}$ each at about 1 ppm level. It was concluded that, the cell exposed to $\text{PH}_3 + \text{H}_2\text{S}$ mixture degraded somewhat more rapidly than a similar cell that was exposed to PH_3 alone. Similar results were also observed when a cell was exposed to syngas containing AsH_3 and H_2S .

Recently, Trembly *et al.* [18-20] studied the effect of trace levels of HCl, AsH_3 , PH_3 , and H_2Se on the performance of solid oxide fuel cell anodes. The authors observed an immediate but reversible performance loss up to 50% when the electrolyte-supported cells were exposed to 20 and 160 ppm HCl in coal syngas at 800 and 900°C [19]. The authors observed little degradation for AsH_3 concentrations less than or equal to 2 ppm during 100 h of testing at 750 and 800°C [18]. Although PH_3 after 100 h exposure did not affect the fuel cell performance at 5 ppm level, formation of a secondary Ni_3P phase was observed at the anode [20]. Anode supported cells exposed to H_2Se at 5 ppm levels showed an immediate degradation at 750°C [20].

Marina *et al.* [21] and Coyle *et al.* [22] also reported that PH_3 and AsH_3 cause severe degradation in the performance of both anode and electrolyte supported SOFCs at ppm

levels. Irreversible degradation was observed for PH_3 at 0.5 to 10 ppm levels in coal syngas at 700 to 800°C due to bulk nickel phosphide phase formation [23]. Investigation of performance of SOFC in coal syngas containing 0-10 ppm AsH_3 at 700-800°C revealed that the performance loss was due to formation of secondary nickel arsenide phases creating a sharp boundary between the converted and unconverted portions of the anode [22].

Researchers at West Virginia University [24-27] have also investigated the effect of PH_3 and HCl on the performance of Ni-YSZ anode. Zhi *et al.* [27] exposed Ni-YSZ half cells to 20 ppm PH_3 in coal syngas. After 48 h of exposure, the morphology of the Ni-YSZ anode surface significantly changed leading to a reduction in the porosity. Further XRD analysis has revealed that phosphorus has reacted with Ni and Zr, leading to the formation of $\text{Ni}_3(\text{PO})_4$ and ZrP_2O_7 . Dramatic and irreversible performance loss of anode-supported SOFC due to 10 ppm PH_3 in coal syngas via formation of Ni_5P_2 phase formations was observed by Xu *et al.* [25]. Xu *et al.* [24] also reported a steady and irreversible power loss of 3% over 400 h at 800 and 850°C for anode-supported cells exposed to 100 ppm HCl in coal syngas.

2.2 Thermodynamic Equilibrium Calculations

Thermodynamic equilibrium calculations have been performed by several researchers [28-31] to predict the stable forms of the trace elements found inherently in typical coal syngas. The exact identity of the species proceeding from the gasifier to the fuel cell depends primarily on the starting coal composition, the gasifier design and the syngas cleanup technology used. These studies provide useful information in determining which species will form condensed phases and can easily be filtered before entering the SOFC [29] and which of them pose a potential to produce secondary phases with the anode material. However, it is still a point of debate whether or not equilibrium calculations are reliable for such applications given the fact that the equilibrium composition varies widely with respect to the thermodynamic database utilized [21].

Trembly *et al.* [29] conducted a thermodynamic equilibrium analysis to determine the effect of warm gas cleanup system conditions on the trace species partitioning between the vapor and the condensed phases and to identify the form of impurity species in coal syngas. The analysis was carried in two steps: cleanup stage analysis (CSA) and anode reaction analysis (ARA). Results showed that Be, Cr, K, Na, and V trace species form condensed phases under warm gas cleanup conditions and should be removed efficiently before reaching the SOFC anode. The authors also reported that antimony, arsenic, cadmium, lead, mercury, phosphorus, zinc and selenium trace species form vapor phase species and of special interest are antimony, arsenic and phosphorus which have the potential to form secondary phases with Ni in the SOFC anode.

Krishnan *et al.* [32] also performed thermodynamic equilibrium calculations using gas streams representative of an oxygen-blown slugging gasifier. Table 2.1 lists the predicted chemical forms and partitioning of the trace species at different temperature ranges [32].

Table 2. 1: Status of trace impurity species in a coal gas stream [32]

Component	> 1000 °C	400-800 °C	100-400 °C	< 100 °C
As	AsO, As ₂	AsO, As ₄	As ₂	AsH ₃
Be	Be(OH) ₂	Condensed species	Condensed Species	Condensed Species
Hg	Hg	Hg	Hg, HgCl ₂	Hg, HgCl ₂
B	HBO	HBO	HBO	-
V	VO ₂	Condensed species	Condensed species	Condensed species
Se	H ₂ Se, Se, SeO	H ₂ Se	H ₂ Se	H ₂ Se
Ni	NiCl, NiCl ₂	Condensed species	Ni(CO) ₄	Ni(CO) ₄
Co	CoCl ₂ , CoCl	Condensed species	Condensed species	Condensed species
Sb	SbO, Sb ₂	SbO, Sb ₂	Sb ₄	Condensed species
Cd	Cd	Cd	CdCl ₂	Condensed species
Pb	Pb, PbCl ₂	PbS, Pb, PbCl ₂	Condensed species	Condensed species
Zn	Zn	Zn, ZnCl ₂	Condensed species	Condensed species

As can be seen from Table 2.1, although the results may vary with the coal and operating conditions of the gasifier, under cold gas clean up conditions ($<100\text{ }^{\circ}\text{C}$) Be, V, Co, Sb, Cd, Pb and Zn impurity species will form condensed phases and can be removed efficiently. However, under warm/hot gas clean up conditions ($>250\text{ }^{\circ}\text{C}$), Sb, Cd, Pb and Zn trace species will form vapor phase species and may not be captured by the filters. These impurities have a potential to interact with the SOFC anode.

Recently, Martinez *et al.* [33] performed an extensive thermodynamic analysis to examine the effect of impurities found in coal syngas derived from 15 different gasifiers on SOFC anode material. They have also performed the calculations in two steps, namely CSA and ARA, as Trembly *et al.* [29]. Results showed that Cr, V, Zn, Be and Se trace species partition to liquid or solid phases at CSA and thus can be easily filtered whereas Pb, S, Cd, Sb, Cl trace species partitioned between the gas and liquid/solid phases and has a potential to proceed from the gasifier to the SOFC anode. Of those gas phase species As, P and Sb demonstrates a propensity to form secondary phases with Ni anode.

2.3 Porous Media Diffusion Modeling

Diffusion transport inside the porous medium has two components: bulk molecular diffusion where molecular to molecular interaction dominates the transport and Knudsen diffusion where molecular to solid wall interaction dominates the transport. Several different approaches have been developed to evaluate multi-component porous media transport. Ackmann *et al.* [34] investigated mass transport in SOFC cathodes and anodes using a Mean Transport Pore Model (MTPM). Their work showed that for typical SOFC anode operating on reformed methane syngas, neglecting Knudsen diffusion or permeation can result in deviations up to 20%.

Lehnert *et al.* [35] modeled the effect of methane-derived syngas on anode performance to determine the effect of anode structural properties on methane conversion. The model considered molecular, Knudsen, and convective transport via the MTPM, and included

the Water Gas Shift (WGS) and Methane Steam Reforming (MSR) reactions. The kinetics for the MSR and WGS were determined experimentally by Drescher *et al.* [36]. The results from this model showed that porosity and pore size have the most significant control (5-12%) over methane conversion.

Haberman and Young [37] investigated the transport of methane-derived syngas in a 1 mm thick porous SOFC anode. Their model used the Darcy equation to describe convective transport due to pressure gradients and the Stefan-Maxwell equation for bulk gas diffusion. Contributions from Knudsen diffusion was ignored due to an assumed large pore size of 10 μm . The model used the same fuel composition and reforming kinetics as Lehnert *et al.* [35]. Only hydrogen oxidation was considered. The results showed that for a case with reforming, little variation in species concentrations exist through the highly porous support. Results also showed an almost uniform hydrogen production rate in the direction of the thickness of the anode, which was higher at the inlet than the exit by nearly two orders of magnitude. The H_2 production followed the temperature profile, which was also nearly uniform through the thickness of the anode, high at the inlet and significantly lower at the exit due to internal reforming.

Hecht *et al.* [38] used Dusty Gas Model (DGM) for the transport of species through a porous Ni/YSZ cermet, and included a detailed kinetic model for MSR. The authors compared results of the model to experimental results from a hardware configuration that approximated the conditions of a true SOFC. The model incorporated 42 separate reaction mechanisms to account for MSR, WGS, and species surface coverages. The comparison of the model results to experimental results showed overall good agreement in trends and species concentrations.

Gemmen and Trembly [39] investigated the detailed transport of coal syngas through porous Ni-YSZ anode of an SOFC using the Dusty Gas Model (DGM). Methane steam reforming and water gas shift reactions were considered to occur homogeneously inside the anode. A constant ratio of 4 between the currents produced from the electrochemical

oxidations of H₂ and CO was assumed. The analyses of operating pressure ranging from 1 to 15 atm revealed its effect on species profiles, diffusion losses and cell heating.

Suwanwarangkul *et al.* [40], compared Fick's, Dusty Gas and Stefan Maxwell Models for a simple one-dimensional case without bulk chemical reactions and recommended the use of Dusty Gas Model for multi-component systems which is the case for SOFC anodes. Same group [41] also performed experimental and numerical study of an electrolyte supported SOFC operating on coal syngas. A two-dimensional isothermal model of a button SOFC was developed considering simultaneous electrochemical oxidation of H₂ and CO by assuming a constant ratio between the currents produced from each of them and water gas shift reaction. Experimental and numerical results indicated that the lower performance of the cell is due to the carbon formation when operated on coal syngas.

2.4 SOFC Anode Degradation Modeling

While the experimental studies provide guidance on the identification of the impurities in coal syngas and their effects on the performance of Ni-yttria stabilized zirconia (Ni-YSZ) anode of SOFCs, tolerance limits for various impurities are not yet established. At low impurity concentrations, degradation rates are quite slow and long term experiments (more than 1000 h) are required in order to determine the durability of the cell for a given concentration [20]. Models developed based on the knowledge base gained from short term experimental data at relatively higher concentrations can be used to estimate the degradation levels at any concentration and at any time.

There are only a few modeling studies that account for the effects of impurities in the syngas on the SOFC anode [18, 42, 43]. Effects of impurities are studied only for H₂ fuel. Hansen [42] analyzed experimental data on sulfur's impact on SOFC anodes using an isotherm for the sulfur coverage on the Ni surface and proposed a linear relationship between the performance loss and the sulfur coverage. In another study, Zhang *et al.* [43] developed a model for the Pt-based catalyst poisoning induced by fuel impurities for

PEM fuel cell. Although their model can be used to simulate and estimate the chemical and electrochemical reaction rate constants, and make some prediction about the severity of the contamination and the performance recoverability, it has not yet been validated against benchmark experimental data.

In addition to electrochemical performance, structural integrity of SOFC anode is essential for successful long-term operation. Anode-supported SOFCs, in particular, rely on anode cermet as structural support for electrolyte and cathode. SOFC anode is subjected to stresses at high temperature, thermal/redox cycles, and coal syngas contaminants effects during long-term operation. These mechanisms can alter anode microstructure and affect its electrochemical performance and structural properties. Sarantaridis and Atkinson [44] proposed a simplified mechanical model of the stress and damage that are likely to be caused by anode expansion due to redox cycle. The model is applied to anode-supported and electrolyte-supported cell configurations to estimate maximum oxidation strain to avoid damage in each configuration. Recently, Iqbal *et al.* [45] developed a durability model involving thermomechanical and fuel gas contaminant degradation mechanisms to predict the long term structural integrity of the SOFC anode. Model predictions indicated that thermomechanical degradation is greater at the anode/electrolyte interface and increases linearly with time and for the phosphine contaminant, the anode structural degradation starts at the exposed anode surface and penetrates towards the active interface.

Overall, there is a dearth in the literature for numerical models that can predict the long term electrochemical performance and durability of SOFCs exposed to fuels with impurities. In order to formulate remedies for the undesirable effects of these impurities, it is necessary to understand the underlying mechanisms through which the cell performance has deteriorated.

2.5 Objective and Goals

The review presented in the previous section revealed that it is essential to establish maximum tolerance limits for potentially harmful impurity species and lifetime of cells at given impurity levels. Since at low impurity concentrations degradation rates are very slow and long term experiments of at least 1000 h are needed, it is practically impossible to establish these limits for tens of impurity species only by testing. The best possible remedy for this problem is to develop theoretical models that can accurately predict the degradation behavior by optimizing the knowledge base gained from short term testing at relatively higher concentrations. The objective of this study is to develop a physics and chemistry based, verified and validated theoretical model to predict the performance degradation of a SOFC anode due to various levels of impurities present in the coal syngas under a range of operating conditions. The model will provide us with the valuable information regarding the lifetime of the cells with minimum number of long term experiments. The specific goals of this work are to:

1. Use equilibrium calculations to predict the stable forms of impurity species at SOFC operating conditions and also to predict conversion of Ni to secondary phases as a function of time.
2. Formulate a simple yet accurate model for mass transport and heterogeneous reactions inside the Ni-YSZ based anode of an SOFC which includes gas phase diffusion, Knudsen diffusion and surface diffusion.
3. Include trace impurity species transport in the anode model using simple reaction mechanisms.
4. Develop phenomenological models to correlate the anode performance to transport of contaminants inside the anode and predict the performance of the SOFCs upon exposure to syngas contaminants.
5. Calibrate the empirical model parameters using experimental results from the literature.

6. Perform parametric studies using the calibrated phenomenological model to predict the cell life times and tolerance levels of the impurities under various operating conditions.

CHAPTER 3- THERMODYNAMIC EQUILIBRIUM CALCULATIONS

Thermodynamic equilibrium calculations provide a quantitative approach for determining the most stable forms of a system of chemical species. In this study, these calculations are performed specifically for identification of the stable forms of coal syngas impurities under SOFC conditions and their possible interactions with the anode material. In what follows calculation methodology and application to coal syngas impurities under SOFC conditions along with the results and conclusions are presented.

3.1 Calculation Methodology

In the present study, Cantera 1.7 [46], an open-source library of chemical kinetics and thermodynamic equilibrium subroutines, which is capable of solving multiphase equilibrium problems, was employed for calculations. For multiphase equilibrium computations, Cantera uses the Villars-Cruise-Smith (VCS) algorithm which solves the stoichiometric formulation of equilibrium conditions by minimizing the total Gibbs function of the system at the specified temperature and pressure with the constraint of non-negative molar concentrations ($\mathbf{n} \geq 0$) [47]:

$$G(\xi) = \mathbf{n}^T \boldsymbol{\mu} = [\mathbf{n}^0 + \mathbf{N}\xi]^T \boldsymbol{\mu} \quad (3.1)$$

Here G and ξ denote the total Gibbs function of the mixture and the extent of reaction vector, respectively. $\mathbf{n}$ is the vector of mole fractions, $\mathbf{N}$ is the stoichiometric matrix, $\boldsymbol{\mu}$ is the vector of species chemical potentials. The superscripts '0' and 'T' stand for initial condition and transpose, respectively. The details of the numerical procedure utilized in Cantera can be found in [47].

The equilibrium analysis was carried out in two parts. The first part, namely gas phase calculations, is aimed at determining the partitioning behavior of coal syngas impurities between the gas and condensed phases under warm gas cleanup conditions. These calculations also provided an implicit verification of the calculation procedure used in this study by comparing the predictions with those of Trembly et al [29]. As a separate analysis, the effect of SOFC operating conditions on the equilibrium status of phosphorous upon introduction of PH_3 to the simulated coal syngas was also investigated on the gas phase system. In the second part of the study, namely multi-phase calculations, simulations are performed using simulated coal syngas with PH_3 impurity including possible secondary Ni-P species expected to form between the phosphorous impurity and the Ni catalyst found in the anode.

All possible forms of the species in the gas phase and/or in the condensed phase were considered in the calculations. The gas phase species are assumed to obey the ideal gas law and the mixture is treated as an ideal mixture. The condensed phase species are assumed to be either stoichiometric solids or stoichiometric liquids. Thermodynamic data of these species are obtained from various resources available in the literature [48-51] and an extensive database of thermodynamic properties for various possible compounds of impurities and cell materials was compiled.

3.2 Results and Discussion

3.2.1 Gas Phase Equilibrium Calculations

3.2.1.1 Possible Forms of Trace Species in Coal Syngas

In an attempt to determine the trace species that are likely to form and be transported to the SOFC anodes, equilibrium calculations were performed under warm gas cleanup conditions (200-500 °C and 1 atm). All possible forms of the impurity species at the gas phase and the condensed phase were considered. Tables 3.1 and 3.2 tabulate the initial concentration of the coal syngas and the impurity species used for the analysis, respectively. These concentrations are representative of typical coal syngas (see Table 1.1 for compositions of the raw syngas derived from different types of gasifiers) and are same as those used by Tremblay *et al.*[29]. Resulting forms of the impurity species are given in Table 3.3 for different temperatures.

Table 3. 1: Coal syngas composition used for the equilibrium analysis under warm gas clean-up conditions

Species	Composition (Vol %)
CO	0.287
H ₂ O	0.272
CO ₂	0.118
H ₂	0.293
N ₂	0.03

Table 3. 2: Trace species composition used for the equilibrium analysis under warm gas clean-up conditions [29]

Species	Composition (ppm)
AsH ₃	0.600
PH ₃	1.910
Sb	0.070
Cd	0.011
Be	0.025
Cr	6.00
Hg	0.025
Se	0.150
Na	320.0
V	0.025
Pb	0.260
Zn	9.00

Table 3. 3: Possible forms of trace species in coal syngas at warm gas clean-up conditions (200-500 °C and 1 atm)

Species	200 °C	300 °C	400 °C	500 °C	800 °C
Arsenic	As(s), As ₄ (g)	As ₄ (g), AsH ₃ (g)	As ₄ (g), AsH ₃ (g), As ₃ Sb (g)	As ₄ (g), AsH ₃ (g), As ₃ Sb (g)	As ₄ (g), AsH ₃ (g)
Phosphorous	HPO ₂ (g)	HPO ₂ (g)	HPO ₂ (g)	HPO ₂ (g)	HPO ₂ (g)
Antimony	SbO ₂ H ₂ (g)	SbO ₂ H ₂ (g)	SbO ₂ H ₂ (g)	SbO ₂ H ₂ (g)	SbO ₂ H ₂ (g)
Cadmium	CdS (s), CdSe (s)	Cd (g), CdSe (s)	Cd (g)	Cd (g)	Cd (g)
Beryllium	BeO (s)	BeO (s)	BeO (s)	BeO (s)	BeO (s)
Chromium	(Na ₂ O)(Cr ₂ O ₃) (s)	(Na ₂ O)(Cr ₂ O ₃) (s)	Cr ₂ O ₃ (s)	Cr ₂ O ₃ (s)	Cr ₂ O ₃ (s)
Mercury	Hg (g)	Hg (g)	Hg (g)	Hg (g)	Hg (g)
Selenium	CdSe (s), PbSe (s)	CdSe (s), PbSe (s)	PbSe (s), H ₂ Se (g), AsSe (g)	H ₂ Se (g), AsSe (g)	H ₂ Se (g)
Sodium	(Na ₂ O)(Cr ₂ O ₃) (s)	Na ₂ CO ₃ (s)	Na ₂ CO ₃ (s)	Na ₂ CO ₃ (s)	Na ₂ CO ₃ (s)
Vanadium	V ₂ O ₃ (s)	V ₂ O ₃ (s)	V ₂ O ₃ (s)	V ₂ O ₃ (s)	V ₂ O ₃ (s)
Lead	Pb (s), PbSe (s)	Pb (s), PbSe (s)	Pb (l), PbSe (s)	Pb (g), Pb (l), PbSe (s), PbSe (g)	Pb (g), PbSe (s), PbSe (g)
Zinc	ZnO (s)	ZnO (s)	ZnO (s)	ZnO (s)	ZnO (s)

As can be seen from Table 3.3, trace species like beryllium, chromium, sodium, vanadium and zinc in coal syngas form condensed phases and can be removed efficiently before reaching SOFC anode whereas antimony, arsenic, cadmium, lead, mercury, phosphorus, zinc and selenium form vapor phase species can react with the anode material. These results conform with those of Tremblay *et al.* [29]. The calculations were repeated at the anode operating conditions and the most stable forms of the impurity

species are also listed in the Table 3.3. As can be seen from the table, antimony, arsenic, cadmium, lead, mercury, phosphorus, zinc and selenium form vapor phase species and have a potential to react with the anode material.

3.2.1.2 Possible Forms of PH_3 in Coal Syngas in the Gas Phase

In addition to calculations at warm gas cleanup conditions, equilibrium calculations were also performed on the gas phase system to check the equilibrium status of phosphorous after PH_3 was introduced into the simulated coal syngas containing 30.6% H_2 , 30.0% CO , 11.8% CO_2 and 27.6% H_2O under SOFC operating conditions. The syngas composition used here is same as that used in the experiments of Zhi *et al.*[26]. Phosphorous containing gas species considered in the present calculations include PH_3 [49], $(P_2O_3)_2$ [49], $(P_2O_5)_2$ [49], HPO [48], HPO_2 [51], HPO_3 [51], CHP [49], CP [49], P_2 [49], P_4 [49], PH [49], PH_2 [49], PO [49], PO_2 [49] and condensed phases include H_3PO_4 (s) [49], H_3PO_4 (l) [49], $(H_3PO_4)_2(H_2O)$ (s) [48] and $(NH_4)H_2PO_4$ (s) [48] .

The calculations showed that, without inclusion of the thermodynamic data for HPO_2 and HPO_3 , PH_3 mainly converts to $(P_2O_3)_2$ the most stable form of gas phase phosphorous containing species under equilibrium conditions. The equilibrium concentrations of PH_3 and $(P_2O_3)_2$ as a function of the initial PH_3 concentration (1-20 ppm) and the system temperatures (750-900°C) are shown in the phase diagram represented by Figure 3.1 (a). As can be seen from the figure, under the equilibrium condition, the major form of phosphorous in the gas phase is $(P_2O_3)_2$, which indicates that most of PH_3 is oxidized due to the presence of high-concentration water vapor in the fuel gas. This is in agreement with the results reported in the literature [20]. It can also be seen from the figure that, the equilibrium concentration of $(P_2O_3)_2$ strongly depends on the initial concentration of PH_3 but not on the temperature in the range of 750 °C - 900 °C.

Inclusion of the thermodynamic data for HPO_2 and HPO_3 to the calculations leads to the major phosphorus species to become HPO_2 and $(P_2O_3)_2$ for a range of temperatures and

PH₃ concentrations relevant to syngas SOFCs. Figure 3.1 (b) illustrates the phase diagram showing equilibrium concentrations of HPO₂ and (P₂O₃)₂ as a function of the initial PH₃ concentration (1-20 ppm) and the system temperatures (750-900°C). As can be seen from the figure, PH₃ was converted mostly to HPO₂ (g) at operating temperatures above 790°C regardless of the initial PH₃ concentration. However, for temperatures below 790°C, the major forms of the phosphorous impurity at equilibrium are HPO₂ (g) and (P₂O₃)₂ (g). This indicates that, the critical temperature where the formation of (P₂O₃)₂ (g) becomes favorable is 790°C.

3.2.2 Multiphase Equilibrium Calculations

Similar calculations have also been performed using simulated coal syngas with PH₃ impurity by including possible condensed phase species anticipated to form between the phosphorous impurity and the Ni catalyst of the anode. Different from gas phase calculations, these calculations include time marching to allow for predicting the nickel conversion (to secondary phases) as a function of time during the operation of SOFC anode. The methodology used is to equilibrate the amount of coal syngas that would pass through the anode in one discrete time step with the amount of Ni present in the cell. After the equilibrium composition is obtained, the gas phase compositions are reset to original (inlet) values but the solid phase species compositions are kept the same as those obtained from the previous time step and the system is allowed to equilibrate again. This is akin to replacing the spent fuel with a fresh batch of fuel after each time step whereas Ni in the anode and its secondary phases never leave the system. The effect of current density was introduced by adding the amount of H₂O/CO₂ produced and removing the amount of H₂/CO reacted proportional to the current, within the discrete equilibrium time step.

(a)

(b)

Figure 3. 1: Phase diagram showing the equilibrium concentration (ppm) of phosphorous containing species in coal syngas as a function of the initial PH_3 concentration and the system temperatures for (a) without thermodynamic data of HPO_2 , (b) including thermodynamic data of HPO_2

A numerical time step of 1 s was used assuming everything equilibrates within that time. In order to justify this assumption, the calculation was repeated for a specific case and it was seen that the results did not change when a time step of 10 s was used which means 1 s is enough for equilibrium (see Appendix A for the figure). Calculations are performed such that each fresh batch of fuel stream reacts with the remainder of the Ni from the previous time step, eventually depleting all the available Ni.

Table 3.4 lists the equilibrium composition of phosphorous-containing species at 900°C and 1.0 atm after 48 hours of operation for initial PH₃ concentrations of 10 ppm and 15 ppm. As can be seen from the table, the major form of gas phase species is HPO₂. In addition, independent of the initial concentration, only secondary phase formation observed is Ni₅P₂ (s). However, other researchers [23, 52, 53] report that other phosphides and even phosphates may form under SOFC operating conditions [26]. Marina *et al.* [23] note that equilibrium calculations involving phosphorus species are very sensitive to the species considered in the calculations and the source of the thermodynamic data used so it may not be possible to predict formation of other phosphides with the current thermodynamic data utilized.

Later the effect of system pressure on conversion of nickel to nickel phosphide at different initial PH₃ concentrations was investigated and the results are given in Figure 3.2 at 750 °C and 0.5 amp. It can be seen from Figure 3.2 (a) and (b) that an increase in the initial concentration of PH₃ results in an increase in the rate of formation of solid Ni₅P₂ phase thus accelerating the degradation. These results are consistent with the experimental data where it was shown that increase in contaminant concentrations leads to faster degradation [54]. It can also be seen that, although an increase in system pressure increases overall system efficiency for SOFCs, the equilibrium shifts toward formation of Ni₅P₂ (s) leading to faster degradation at higher operating pressure.

Table 3. 4: Equilibrium composition of phosphorus-containing species at 900°C and 1.0 atm after 48 hours of operation

	10 ppm		15 ppm	
Species	Concentration (ppb)	Moles	Concentration (ppb)	Moles
PH ₃	3.0E-07	4.2E-17	3.6E-07	5.0E-17
(P ₂ O ₃) ₂	2.0E+00	2.8E-10	4.1E+00	5.7E-10
(P ₂ O ₅) ₂	8.7E-26	1.2E-35	1.8E-25	2.5E-35
CHP	2.2E-07	3.1E-17	2.6E-07	3.7E-17
CP	1.6E-21	2.2E-31	1.9E-21	2.7E-31
P ₂	1.7E-16	2.4E-26	2.4E-16	3.4E-26
P ₄	1.2E-35	1.7E-45	2.4E-35	3.4E-45
PH	3.9E-14	5.5E-24	4.7E-14	6.6E-24
PH ₂	1.9E-09	2.6E-19	2.2E-09	3.2E-19
PO	7.2E-10	1.0E-19	8.6E-10	1.2E-19
PO ₂	2.8E-08	3.9E-18	3.3E-08	4.7E-18
HPO	7.2E-06	1.0E-15	8.6E-06	1.2E-15
HPO ₂	2.7E+03	3.8E-07	3.2E+03	4.6E-07
HPO ₃	1.0E-04	1.4E-14	1.2E-04	1.7E-14
Ni ₅ P ₂	-	5.4E-05	-	7.5E-05

Figure 3.3 shows the effect of increasing temperature and current on formation of nickel phosphide phase. It can be seen from the figures that increasing temperature favors the conversion of Ni to Ni₅P₂ (s). Analysis of Figure 3.33 (a) and (b) also reveals that an increase in total current decreased the amount of Ni₅P₂ (s) formed as opposed to the experiments [26]. The reason for this discrepancy can be attributed to equilibrium calculations not taking into account of chemical kinetics.

Tremblay et al. [29] also performed similar calculations considering interactions of As, P, and Sb impurities with Ni catalyst of the SOFC anode. Different from the current study,

the authors analyzed thin sections at the inlet and outlet edges of the anode rather than considering whole anode. In addition, the amount of nickel equilibrating with the coal syngas with impurities was taken as constant for each calculation allowed to equilibrate for 1, 100, 500, 1000, 3000 and 10,000 h. This approach overpredicts the amount of secondary phases formed with the Ni catalyst since it neglects the amount of Ni converted in the previous calculation. In other words, in each calculation the impurity species equilibrate with the same amount of Ni.

3.3 Summary and Conclusions

Gas phase equilibrium calculations were performed to determine the partitioning behavior of coal syngas impurities between the gas and condensed phases under warm gas cleanup conditions and to identify the effect of SOFC operating conditions on the equilibrium status of phosphorous upon introduction of PH_3 to the simulated coal syngas. Following conclusions can be drawn from gas phase equilibrium calculations:

- Under warm gas cleanup conditions (200-500°C and 1 atm), trace species like Be, Cr, K, Na, and V in coal syngas form condensed phases and can be removed efficiently before reaching SOFC anode. However, Sb, As, Cd, Pb, Hg, P, Zn and Se form vapor phase species can react with the anode material
- Under the equilibrium conditions, the major form of phosphorous in the gas phase was HPO_2 (g) at operating temperatures above 790°C. For temperatures below 790°C, the major forms of the phosphorous impurity at equilibrium are HPO_2 (g) and $(\text{P}_2\text{O}_3)_2$ (g) indicating the critical temperature where formation of $(\text{P}_2\text{O}_3)_2$ (g) becomes favorable is 790°C.
- For temperatures above 790°C, the equilibrium concentration of HPO_2 (g) depends heavily on the initial concentration of PH_3 but much less dependent on the temperature.

(a)

(b)

Figure 3. 2: Effect of pressure on nickel to nickel phosphide conversion at different initial PH_3 concentrations at 750 °C and 0.5 amp

(a)

(b)

Figure 3. 3: Effect of current at different temperatures to nickel to nickel phosphide conversion for 15 ppm initial concentration of PH_3 at 1 atm

Similar calculations have also been performed using simulated coal syngas with PH_3 impurity to predict the activity of phosphorous in coal syngas by formation of specific Ni-P solid phases and it was concluded that:

- Only secondary Ni_5P_2 (s) phase formation was observed for all temperatures, pressures, initial impurity concentrations and currents analyzed during this study as opposed to some where the majority of Ni was found to convert to $\text{Ni}_3(\text{PO}_4)_2$ (s) or other forms of phosphides such as Ni_2P and Ni_3P .
- Increase in initial PH_3 concentration and temperature increased the rate of formation of Ni_5P_2 (s) thus accelerating the degradation process
- Increase in system pressure increases overall system efficiency of SOFCs however at higher pressures the equilibrium shifts toward formation of Ni_5P_2 (s).
- Increase in total current decreased the amount of Ni_5P_2 (s) formed as opposed to the experiments possibly due to neglecting chemical kinetics.

CHAPTER 4- MULTI-COMPONENT DIFFUSION INSIDE POROUS ANODE

This chapter is organized as follows. Section 4.1 presents a brief overview of the models for multi-component diffusion in porous media that are used in the literature. Section 4.2 and 4.3 describe the model equations used for the current study and the numerical solution method used for solving these model equations, respectively. Section 4.4 presents the implicit verification of the model by comparing its predictions against an independent numerical solution for the same problem. Section 4.5 introduces a correction for the multi-component effective diffusivity and the results from application of this correction to syngas transport through the porous anode. Section 4.6 provides the summary and conclusions for this study.

4.1 Overview

The performance of a SOFC at high operating current densities is reduced mainly due to the mass transport losses, that is, the demand for reactants exceeds their capacity to diffuse through the porous anode to the reaction site at the anode-electrolyte interface. The multi-component mass transport in SOFC anodes is also coupled with the bulk chemical reactions and the resulting diffusion and reaction time scales of different species dictate the limiting behavior. Accurate modeling of this phenomenon is imperative for development of better fuel cell designs.

The equations governing the multi-component mass transfer include Stefan-Maxwell relations for calculation of species fluxes. These relations are coupled, nonlinear system of partial differential equations and are cumbersome to solve, especially when a large number of species are involved as in the case of coal syngas. Alternatively, simple Fick's Law type relations with an effective multi-component diffusivity are generally used to model the diffusion fluxes [55-58]. Advantages of using Fick's Law type of relations Stefan-Maxwell relations include simplicity of implementation since they can be directly substituted to the species conservation equation and requirement of less computation time. The latter is especially important when the species conservation equation is solved in conjunction with other governing equations for momentum and heat transfer, as is the case of 3-D modeling of Solid Oxide Fuel Cells. However, the validity of such simplified models is not well established.

In this study, these two approaches are compared by simulating mass transfer inside an SOFC anode operating on coal syngas consisting of CH_4 , H_2 , CO , H_2O , CO_2 and N_2 . A two-dimensional computer code was developed for the solution of models based on Stefan-Maxwell and Fick's Law flux relations to predict the species concentration distribution inside the porous anode. Methane steam reforming and water gas shift reactions are taken into account in addition to the electrochemical reactions at the anode/electrolyte interface and chemical kinetics modeling was employed for the bulk reactions. The ratio between the current produced by CO and H_2 oxidation is assumed to be constant.

4.2 Model Equations

Diffusion transport inside the porous medium has two components: bulk molecular diffusion where molecular to molecular interaction dominates the transport and Knudsen diffusion where molecular to solid wall interaction dominates the transport.

Several different approaches have been developed to evaluate multi-component porous media transport [57, 59, 60]. In the present study, Stefan-Maxwell Model (SMM) and Fick's Model (FM) both of which include the effect of Knudsen diffusion in addition to the bulk molecular diffusion were used.

The flux expression in Stefan-Maxwell model is given by [61]:

$$\frac{N_i}{D_i^{k*}} + \sum_{\substack{j=1 \\ j \neq i}}^n \frac{y_j N_i - y_i N_j}{D_{ij}^*} = -\frac{P}{RT} \nabla y_i \quad (4.1)$$

where N_i and y_i are the molar fluxes and mole fractions of species, D_{ij}^* and D_i^{k*} are the effective binary and Knudsen diffusivities. The first term on the left hand side accounts for the Knudsen diffusion and the second one signifies the multi-component bulk molecular diffusion.

The effective binary diffusivity is usually defined as:

$$D_{ij}^* = \frac{\varepsilon}{\tau} D_{ij} \quad (4.2)$$

where ε and τ are the bulk porosity and tortuosity, respectively. D_{ij} is the binary diffusivity and can be calculated using Chapman- Enskog relations [61]:

$$D_{ij} = 0.001858 \frac{\left[T^3 (M_i + M_j) / M_i M_j \right]^{1/2}}{P \sigma_{ij}^2 \Omega_D} \quad (4.3)$$

where T and P are the temperature and the pressure of the system, respectively. M_i represents the molecular weight of species i . σ_{ij} is given by

$$\sigma_{ij} = \frac{\sigma_i + \sigma_j}{2} \quad (4.4)$$

σ_i is the collision diameter of species i . The dimensionless parameter Ω_D is the collision integral calculated as

$$\Omega_D = \frac{A}{T_N^B} + \frac{C}{\exp(DT_N)} + \frac{E}{\exp(FT_N)} + \frac{G}{\exp(HT_N)} \quad (4.5)$$

where the coefficients A, B, C, D, E, F, G, H are 1.06036, 0.1561, 0.193, 0.47635, 1.03587, 1.52996, 1.76474, 3.89411, respectively [62]. The dimensionless temperature T_N is defined as:

$$T_N = \frac{kT}{\varepsilon_{ij}} \quad (4.6)$$

where k is the Boltzmann constant. The term ε_{ij} is calculated as

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} \quad (4.7)$$

where ε_i is the characteristic Lenard-Jones energy of species i .

Likewise Knudsen diffusivity is defined as:

$$D_i^{k*} = \frac{\varepsilon}{\tau} \langle r \rangle \frac{2}{3} \sqrt{\frac{8RT}{\pi M_i}} \quad (4.8)$$

where $\langle r \rangle$ is the mean pore radii and R is the universal gas constant .

Fick's Model (FM), a simpler method used to describe the transport of species in the gas phase, is defined as:

$$N_i = -D_i^{eff} \frac{P}{RT} \nabla y_i \quad (4.9)$$

where D_i^{eff} is the effective diffusivity. Simulations with Fick's Model were conducted by using the effective multi-component diffusivity proposed by Yakabe *et al.* [57]:

$$D_i^{eff} = \frac{\varepsilon}{\tau} \left[\frac{1 - \alpha_{i,m} y_i}{D_{i,m}} + \frac{1}{D_i^k} \right]^{-1} \quad (4.10)$$

$\alpha_{i,m}$ is a dimensionless parameter given by:

$$\alpha_{i,m} = 1 - \left(M_i / M_{avg} \right)^{1/2} \quad (4.11)$$

where M_{avg} is the average molecular weight and M_i is the molecular weight of the species i . Multi-component molecular diffusivity of species i in the mixture $D_{i,m}$ is given by

$$D_{i,m} = \frac{1 - y_i}{\sum_{j \neq i} \frac{y_j}{D_{ij}}} \quad (4.12)$$

The calculated molar fluxes either from SMM (Eq.(4.1)) or from FM (Eq.(4.9)) are then used to determine the rate of change of species concentrations through the following conservation equation:

$$\varepsilon \frac{P}{RT} \frac{\partial y_i}{\partial t} = -\nabla N_i + R_i \quad (4.13)$$

where R_i is the molar rate of production of species i due to bulk chemical reactions.

In the present study, the principle bulk chemical reactions of concern are methane steam reforming and water gas shift reactions, described respectively as:

where k_r^+ and k_r^- are the forward and backward reaction rate constants for reforming reaction and k_s^+ and k_s^- are the reaction rate constants for shift reaction. Experimentally determined values for these rate constants and their Arrhenius form can be found in [63, 64]. The net reaction rates are given for reforming and shift reactions, respectively as:

$$R_r = k_r^+ p_{CH_4} p_{H_2O} - k_r^- p_{CO} (p_{H_2})^3 \quad (4.16)$$

$$R_s = k_s^+ p_{CO} p_{H_2O} - k_s^- p_{CO_2} p_{H_2} \quad (4.17)$$

where P_i is the partial pressure of species i .

4.3 Numerical Solution Method

A finite volume method is used to discretize the governing equation given in Eq. (4.13). Crank-Nicholson method is used for time discretization but source terms are treated fully explicit. The specified boundary conditions are the species concentration at the anode fuel channel interface and molar fluxes at anode electrolyte interface proportional to the prescribed cell current. It is assumed that there is zero flux of species at the two side walls. The ratio between the current produced by CO and H₂ electrochemical oxidation is assumed to be constant and taken as 4 for the current study [65].

4.4 Model Validation

As explained in the section 4.2, Stefan Maxwell Model (SMM) and Fick's Model (FM) are the two of the models which are used to calculate the fluxes of each species in a multi-component system. Here these two approaches were compared by simulating mass transfer inside an SOFC anode operating on coal syngas consisting of CH_4 , H_2 , CO , H_2O , CO_2 and N_2 . A two-dimensional computer code was developed for the solution of models based on Stefan-Maxwell and Fick's Law flux relations to predict the species concentration distribution inside the porous anode. A schematic representation of the SOFC anode used for this study is shown in Figure 4.1.

Figure 4. 1: Schematic representation of the SOFC anode

The predictive ability of the developed code is verified by comparing the results of molar formation rates to those of [35] that also used SMM to predict the species molar fluxes for an identical case. The syngas composition used is 2.9 % CO , 2.63 % H_2 , 0.44 % CO_2 , 4.93 % H_2O and 1.71 % CH_4 . Table 4.1 summarizes the parameters used for comparison.

Table 4. 1: Parameters used for comparison

Parameter	Value
Anode Thickness (mm)	2.0
Temperature (°C)	850
Current Density (A/cm ²)	0.3
Mean pore diameter, $\langle r \rangle$ (μm)	1.07
Operating temperature (K)	1123
Tortuosity	3.6
Porosity	0.56

Figure 4.2 shows a good agreement between two independent calculations which indicates the model was successfully implemented.

Figure 4. 2: Comparison between the molar rate of formation results of the present study and those of [35]

4.5 Correction of Effective Diffusivity

The 2-D code validated above is then used to compare the results obtained using Fick's model for diffusion flux with those obtained using Stefan-Maxwell model. Figure 4.3 shows the maximum percentage difference (deviation from SMM predictions of concentration) of Fick's Model vs. current density.

Figure 4. 3: Maximum percentage difference of Fick's model versus current density for (a) reactants, (b) products

As can be seen from the figure, at low current densities the models agree well but as current increases the differences increase to up to 20 % at a current density of 4 A/cm². The difference in the Fick's Law model is positive for the fuel species (reactants) and negative for the products. Based on these findings an empirical correction is proposed for the effective diffusivity used in Fick's law model as:

$$D_i^{eff*} = D_i^{eff} \left(1 \pm c \frac{i}{i_{ref}} \right)^n \quad (4.18)$$

where i is the total current density and i_{ref} is the reference current density taken as 1 A/m². The sign in the equation is taken as (+) for reactants (H₂ and CO) and (-) for

products (H_2O and CO_2). Model parameters c and n are found as 4.88×10^{-4} and 2, respectively, by calibrating it with the SMM using the two-dimensional code presented here.

The corrected diffusivities were used to predict the species concentration distribution inside an SOFC anode running on coal syngas. Anode was treated as a two-dimensional medium. Tables 4.2 and 4.3 show the syngas composition and the anode electrode properties used for simulations.

Table 4. 2: Coal syngas composition

Species	Mole Fractions
CO	0.291
H_2	0.285
CO_2	0.118
H_2O	0.276
CH_4	0.021
N_2	0.009

Table 4. 3: Anode Properties

Parameter	Value
Thickness (mm)	0.5
Width (mm)	0.542
Tortuosity	3.6
Porosity	0.56
Mean pore diameter, $\langle r \rangle$ (μm)	1.07
Operating temperature (K)	1123

Mole fraction distributions inside the porous anode directly below the fuel channel is given in Figures 4.5 and 4.6 for operating current densities of 1 A/cm^2 and 4 A/cm^2 , respectively. As can be seen from the figures the corrected diffusivity coefficient gave better agreement with the Stefan-Maxwell model and even at higher current densities the error is less than 5 % (see Figure 4.4). Since this correction is based on numerical experiments it is expected to have some errors and 5 % error is acceptable for such a heuristic model.

Figure 4. 4: Concentration profiles along the anode thickness predicted by FM and SMM for (a) CO , (b) H_2 , (c) CO_2 and (d) H_2O at 1 A/cm^2

Figure 4. 5: Concentration profiles along the anode thickness predicted by FM and SMM for (a)CO (b)H₂ (c)CO₂ and (d)H₂O at 4 A/cm²

The estimated reaction and diffusion time scales for the conditions used in the above simulation normalized with the flow through time ($\tau_{conv} = L/u = 0.267$ s with L being fuel channel length and u being average velocity inside the channel) of the fuel in the gas channel are given in Tables 4.4 and 4.5 respectively. It can be seen from Table 4.4 that there is ample time for the component species to diffuse through the anode as they flow through the gas channel. Normalized reaction time scales (Table 4.5) indicate that, with the given inlet concentrations, steam methane reformation mostly proceeds in the forward

direction whereas as water gas shift reactions may proceed in both directions. Moreover diffusion time scales are much smaller compared to reaction time scales indicating that this electrode is not limited by diffusion.

Table 4. 4: Normalized diffusion time scales

Species	$\tau_{\text{diff}}/\tau_{\text{conv}}$
CO	0.030486
H ₂	0.008841
CO ₂	0.038900
H ₂ O	0.025321
CH ₄	0.028375

Table 4. 5: Normalized reaction time scales

	$\tau_{\text{chem}}/\tau_{\text{conv}}$	
	Forward	Backward
Steam Methane Reforming	0.169621	1570.154
Water Gas Shift	0.069015	0.048962

4.6 Application: Button Cell

In order to independently verify the proposed corrections to the effective diffusivities used in Fick's law type models applied to the multi-component mass transfer problems in fuel cells; this approach is employed in a three dimensional simulation of a real button cell. The model used for these simulations is described elsewhere [66, 67] in the literature and will not be covered here. The salient features of the model are that it allows for several species and bulk-reactions on the anode side and it handles the simultaneous electrochemical oxidation on CO and H₂ without assuming a constant ratio between the current produced by each; rather this ratio is an outcome of the model (see ref. [68]). Also, the diffusion fluxes are calculated using Fick's law type relations and the effective diffusivities are calculated using the model in Eq. (4.10). The button cell simulated here is modeled after the experiments being performed at WVU [69]. The active area of the button cell is approximately 2 cm². The anode, electrolyte and cathode thicknesses are 780 μm, 20 μm and 200 μm respectively. The fuel stream fed to the anode has the composition shown in Table 4.6. The cathode side is supplied with air (21% O₂ and 79% N₂). Both air and fuel streams are supplied at a temperature of 800 °C. The flow field around the button cell is not included in the computation domain. However, its effect on the cell is taken into account using appropriate boundary conditions and transport properties. Given the low utilization of fuel and air in the button cell experiments, it was found that the current density distribution inside the cell was uniform at all currents.

Table 4. 6: Fuel composition supplied to the anode

Species	H ₂	CO	CO ₂	H ₂ O
Mol fraction	0.303	0.229	0.209	0.259

Figure 4.6 shows the experimentally measured and numerically computed VI curves for the button cell. Computations are performed both with and without the proposed correction to the effective multi-component diffusion coefficients.

Figure 4. 6: Experimental and numerically simulated VI curves for the button cell

It can be seen from the figure that the agreement between the experiments and numerical predictions is good for low cell currents but at high currents the computations without correction to the diffusion coefficients fail to predict the onset of diffusion limitation of the cell performance. However the numerical results with corrected diffusion coefficients accurately predict the limiting current though the agreement in terms of voltage values is poor near the limiting current region of the VI curve. It should be noted that a reasonable value of 2.5 [70, 71] is used for tortuosity in these simulations. Though some researchers [72, 73] use higher values for tortuosity to calibrate diffusion limitation, they are not believed to be physically realistic [70, 74]. For a thorough analysis, the simulations were repeated with a higher tortuosity of 10 with and without correction and the resulting VI curves are also plotted in Figure 6. It can be seen that, although the voltages for $\tau=10$ are lower than those for $\tau=2.5$, the curve does not show the typical drop in voltage at high currents when no correction was applied. When the correction was applied with $\tau=10$,

the cell limiting current was found to be much lower than the experimentally observed value. It may thus be concluded that the inability of most numerical models to accurately predict the diffusion limitation is due to the inaccuracy resulting from Fick's law type diffusion model rather than the uncertainty in the tortuosity values. The limiting behavior is known to be due to the concentration of the reactants becoming very small near the active electrolyte/electrode interface.

4.7 Summary and Conclusions

Stefan-Maxwell Model (SMM) and simple Fick's Model (FM) type of relations both including Knudsen diffusion for the calculation of species mole fractions in a multi-component systems were compared and it was found that at low current densities the models agree well but as current increases the differences also increase. Based on the findings an empirical correction is proposed for the effective diffusivity used in Fick's Model. The corrected diffusivity coefficient gave better agreement with the Stefan-Maxwell model and even at higher current densities the error is less than 5 %. As an application, an SOFC button cell which is being tested at West Virginia University was simulated. Numerical simulations with the corrected diffusivity accurately predicted the limiting current even with a reasonable tortuosity of 2.5. However, the predicted voltages were slightly different from the experimental values near the limiting current region.

CHAPTER 5- IMPURITY DEGRADATION MODEL

This chapter describes the underlying mathematical relations used for modeling the degradation phenomena for the Ni-YSZ based SOFC anodes due to contaminants in coal syngas. In what follows, description of the model along with the model equations is presented. Calibration of the model and predictions using the calibrated model are presented in later sections of the chapter.

5.1 Overview

The performance and durability of SOFC operating on coal syngas is affected by the impurities such as phosphorus, arsenic, zinc, sulfur, mercury, selenium, and vanadium. It is difficult to completely remove these impurities and the clean-up processing could be very expensive. Therefore, it is imperative that fuels cell be tolerant to these impurities up to a certain level. While there are some experimental studies [18-20, 75-79] in the literature on the identification of impurities in coal syngas and their effects on the performance of Ni-Yttria stabilized Zirconia (Ni-YSZ) anode of SOFCs, tolerance limits for various impurities are not yet established. Present targets for levels of impurities in coal syngas for SOFC applications set by U.S. Department of Energy [80] are: total S < 60 ppbv, total halides < 100 ppbv, As < 5ppbv, Se < 0.2 ppmv and Cd < 30 ppbv. At low impurity concentrations, degradation rates are quite slow and long term experiments (more than 1000 h) are required in order to determine the degradation rates in a cell [20]. Theoretical models that accurately predict the degradation behavior of SOFCs operating on syngas with very low levels of impurities could significantly reduce the time and

effort involved in durability experiments. In order to formulate remedies for the undesirable effects of these impurities, it is necessary to understand the underlying mechanisms through which the cell performance has deteriorated.

In this study, a novel one-dimensional model is developed to predict the typical degradation patterns observed for contaminants such as P and As. It is widely reported that these species form secondary phases with Ni [21, 29]. The deposition of the impurity on the Ni catalyst starts near the fuel channel/anode interface and slowly moves toward the active anode/electrolyte interface. Figure 5.1 shows SEM images of the contaminant coverage along the anode thickness after 990 h of exposure to PH_3 at different concentrations. It can be seen from the figure that upon exposure to the contaminants, there are two distinct regions of anode; one where the catalyst has formed secondary phases with the contaminant and one where the impurity has apparently not yet reached.

Figure 5. 1: Penetration thickness after 990 h with 1, 2, 5 and 10 ppm of PH_3 in coal syngas ([21], used with permission from PNNL)

Figure 5.2 shows a typical performance degradation curve for an SOFC exposed to syngas with H₂Se impurity. It should be noted that, in this study, to obtain a first-order comparison between the experimental results from various researches, a plot of the modified cell power density versus the operating time was used. The modified cell power density, P*, is defined by

$$P^* = P_{\text{ref}} - \left(\frac{P_0 - P}{P_0} \right) \quad (5.1)$$

where P_{ref} is the reference power density taken as 1, P_0 is the power density at the time when the trace species is introduced and P is the power density at any time.

Figure 5. 2: Typical degradation curve for 1 ppm H₂Se in coal syngas at 700 °C [81]

As can be seen from the figure, performance degradation with time, in general, has four distinct stages, namely initial performance drop, intermediate slow degradation, second

fast degradation and final slow degradation. It is postulated that four stages of typical degradation behavior can be correlated with the penetration of the catalyst secondary phase into the anode. Initial performance drop and intermediate slow degradation happen as the secondary phase front moves slowly toward the active interface. Eventually, when the front reaches the active interfaces, the catalyst at the active interface becomes deactivated leading to second fast degradation. After the catalyst is converted to the secondary phases to the maximum possible extent, the performance, if the cell is not completely dead, more or less stabilizes at a low value. The model presented in the current work attempts to capture the type of behavior discussed here both in terms of secondary phase formation and penetration and performance degradation.

The model includes gas diffusion including Knudsen diffusion and surface diffusion within the anode and the adsorption/desorption reactions on the surface of the Ni-YSZ based anode. The model parameters are calibrated to match the degradation rates reported in the literature.

Many details were disregarded to ensure model simplicity and applicability to many coal syngas impurities. However, the apparent subject complexity is still adequately represented by the resulting simplified model. Main assumptions made in the development of the model are:

- A competitive adsorption mechanism is assumed between the contaminant(s) and H_2 gas.
- The base line cell performance degradation due to natural aging of cell materials is assumed to be small in comparison to the degradation caused by impurity effects on the anode.
- CO is not supporting the current production but it is indirectly contributing by augmenting the H_2 supply through water gas shift reaction
- Interaction between the solid YSZ and the gas phase species is neglected since it is presumed that the degradation occurs due to secondary phase formation between the impurity species and the Ni catalyst.
- Diffusion like one-dimensional transport of coverages is assumed.

- Monolayer adsorption mechanism is adopted.
- Local porosity and electrical conductivity are functions of local impurity coverage.
- Exchange current density is a function of impurity coverage at the active anode/electrolyte interface.

5.2 Model Equations

The degradation model employed in this study considers the competitive adsorption of H₂ and the typical impurity X on the surface of Ni catalyst. The proposed monolayer adsorption mechanism is given by:

This mechanism is called monolayer adsorption mechanism since it is assumed that once an active catalyst site is taken up by either H₂ or contaminant X, it is not accessible for other species until it is released by the original occupying species. Also in the model, the sites that are covered by X and are not subsequently released are assumed to eventually form secondary phases. The composition and nature of the secondary phases are not resolved by this model.

Based on the observation that the front of the coverage moves with time, a one dimensional phenomenological transport equation for the coverage (of species *i*) propagation along the thickness of the anode can be written as:

$$\frac{\partial \theta_i}{\partial t} = D_\theta \frac{\partial^2 \theta_i}{\partial z^2} + \omega_{\theta_i} \quad (5.4)$$

where θ_i is a progress variable here representing the surface coverage for species i which is defined as the fraction of the catalyst sites that is covered by the adsorbed species. D_θ is the transport coefficient for the progress variable and taken as $1 \times 10^{-9} \text{ m}^2/\text{s}$. ω_{θ_i} denotes the source terms due to the reactions given in Eq.s (5.2) and (5.3), that is

$$\omega_{\theta_X} = k_{f,X} y_X \theta_{Ni} - k_{b,X} \theta_{Ni-X} \quad (5.5)$$

$$\omega_{\theta_{Ni-H}} = k_{f,H} y_{H_2} \theta_{Ni}^2 - k_{b,H} \theta_{Ni-H}^2 \quad (5.6)$$

where k_f and k_b are the forward and backward reaction rate constants. y_i is mole fraction of the species i . As a further constraint the surface coverages for the contaminant, hydrogen and nickel must add up to 1:

$$\theta_{Ni-X} + \theta_{Ni-H} + \theta_{Ni} = 1 \quad (5.7)$$

The diffusion constant and the forward and backward reaction rate constants for the impurity adsorption in Eq.s (5.5), (5.6) and (5.7) are the parameters that need to be estimated using the available experimental data.

Source terms found from Eq.s (5.5) and (5.6) are used to calculate the gas phase concentration distribution along the thickness of the anode from one-dimensional species conservation equation for porous media given by:

$$\varepsilon \frac{P}{RT} \frac{\partial y_i}{\partial t} = \frac{\partial}{\partial z} \left(\frac{P}{RT} D_i^{eff} \frac{\partial y_i}{\partial z} \right) + R_i + S_i \quad (5.8)$$

where D_i^{eff} is the effective diffusivity for species i in the mixture including both Knudsen and binary diffusivities detailed calculation of which is given in Chapter 4.2. R_i is the molar rate of productions of species i due to water gas shift and methane steam reforming reactions defined by Eqs. (4.16) and (4.17). Since adsorption of the contaminant on the catalyst eventually forms secondary phases that cause morphological changes thereby

reducing the pore sizes, it is postulated that local porosity, and hence the effective diffusivity, is a function of local contaminant coverage via

$$\varepsilon = \varepsilon_0 (1 - \theta_{Ni-X})^p \quad (5.9)$$

where ε_0 is the porosity at zero contaminant coverage.

S_i in Eq. (5.8) is the net production rate of species i which is calculated from:

$$S_i = \dot{\omega}_{\theta_i} \Gamma a_s \quad (5.10)$$

The site density, Γ , (mol/m^2) is the number of active catalyst sites per unit interfacial area between the solid and gas phases of the porous electrode and specific catalyst area and, a_s , ($1/\text{m}$) is the ratio of interfacial area per unit volume of the anode. These two parameters are obtained from literature [82] and are taken as $\Gamma = 2.6 \times 10^{-5} \text{ mol}/\text{m}^2$ and $a_s = 2.0 \times 10^5 \text{ m}^{-1}$.

Performance curve is obtained by subtracting the voltage losses, i.e. overpotentials, from the theoretical Nernst voltage. Nernst voltage is calculated from

$$E_N = -\frac{\Delta G^o}{2F} - \frac{R_u T}{2F} \ln \left[\frac{y_{H_2O}}{y_{H_2} y_{O_2}^{1/2}} \right] \quad (5.11)$$

where, F is the Faraday's constant, R_u is universal gas constant, T is the temperature, and y_{H_2} and y_{H_2O} are the mole fractions of hydrogen and water vapor on the anode side and y_{O_2} is the mole fraction of oxygen on the cathode side. ΔG^o is the Gibbs function for oxidation of hydrogen

Concentration overpotential or mass transfer loss due to bulk diffusion resistance is given as:

$$\eta_{diff} = \frac{R_u T}{2F} \ln \left[\frac{P_{H_2}^{A/E} P_{H_2O}^{A/F}}{P_{H_2}^{A/F} P_{H_2O}^{A/E}} \right] \quad (5.13)$$

where P_i is the partial pressure of the species i . Subscripts A/E and A/F denote the anode/fuel channel and anode/electrolyte interfaces, respectively.

Activation loss due to adsorption of contaminant on the active sites for electrochemical reactions is calculated from Butler-Volmer equation with the assumption that the transfer coefficient α is 0.5

$$\eta_{act} = \left[\frac{2\alpha F}{R_u T} \right]^{-1} \sinh^{-1} \left(\frac{i_{H_2}}{2i_{o,H_2}} \right) \quad (5.14)$$

where i_{H_2} is the current density. Exchange current density, i_{o,H_2} is usually a function of temperature and the hydrogen activity at the active interface. Here it is postulated that the catalyst deactivation at the interface due to contaminant coverage will also affect the exchange current density. The proposed equation to model the combined effect is given by

$$i_{o,H_2} = c_1 \left(\frac{y_{H_2,int}}{y_{H_2,ref}} \right) \exp \left(-\frac{E_{act,H_2}}{R_u T} \right) (1 - \theta_{Ni-X,int}^m)^n \quad (5.15)$$

where the reference concentration, $y_{H_2,ref}$, is 0.333, the activation energy barrier, E_{act,H_2} , is 91.661 kJ/mol, and the constant c_1 is 3.936×10^7 [83]. Subscripts m and n are the model parameters obtained from calibration with the experimental data. Use of a power law type of relation in Eq.(5.15) may seem like an arbitrary choice with no chemical or physical reasoning .However, this type of curve fit used in this engineering model is the

best option for capturing all four stages of the typical degradation curve shown in Figure 5.2. Similar approaches are widely used in the literature, for example, as in the case of using Arrhenius type of relation for explaining the temperature dependence of the chemical reaction rate constants.

The charge conservation equation is written as

$$\frac{1}{c} \frac{\partial \phi}{\partial t} = 0 = \frac{\partial}{\partial z} \left(\sigma \frac{\partial \phi}{\partial z} \right) \quad (5.16)$$

Since formation of secondary phases alters the electrical conductivity, σ , of the anode, it can be modified and written as a function of the local contaminant coverage:

$$\sigma = \sigma_0 (1 - \theta_{Ni-X})^q \quad (5.17)$$

where σ_0 is the electrical conductivity at zero percent coverage of the contaminant. Subscript q is a model parameter determined via calibration with the experimental data. Again a similar reasoning apply in selection of this power law as that in Eq. (5.15).

Eq.(5.16) is solved with the following boundary conditions:

$$1) \text{ At Anode/Fuel Channel Interface: } \phi = 0 \quad (5.18)$$

$$2) \text{ At Anode/Electrolyte Interface: } -\sigma \frac{\partial \phi}{\partial z} = i \quad (5.19)$$

where i is the current density. Ohmic loss in the anode resulting from electrical conduction loss due to adsorption of the contaminant thereby changing the conductive properties of the catalyst surface is then calculated as

$$\eta_{ohm} = \Delta \phi_{anode} \quad (5.20)$$

Here $\Delta\phi_{anode}$ is the potential difference across the anode.

5.3 Numerical Method

The numerical model integrates the one-dimensional unsteady diffusion Eqs. (5.4) and (5.8) using finite volume method. The diffusion terms are advanced implicitly by Crank-Nicholson scheme whereas the source terms are treated fully explicitly. The diffusion terms are spatially discretized using second order central differencing scheme. The one-dimensional computational domain measures from 0 to L where L is the anode thickness. The simulations were run on a uniformly distributed grid typically composed of 19 cells with a typical constant time step Δt of 1×10^{-5} s.

At the upper and lower boundaries corresponding to anode/fuel channel and anode/electrolyte interfaces, respectively, zero-flux boundary conditions were imposed for coverages in Eq. (5.4). As for Eq. (5.8), constant molar fluxes proportional to the prescribed cell current are employed at anode/electrolyte interface. At the anode/fuel channel boundary, the diffusive flux is set equal to the convective flux given by

$$-D_i^{eff} \left. \frac{\partial y}{\partial z} \right|_{z=0} = k_m (y_\infty - y_{surface}) \quad (5.21)$$

where y_∞ is the free stream concentration at the fuel channel, $y_{surface}$ is the surface concentration at the cell wall. k_m is the mass transfer coefficient calculated from Sherwood number ($Sh = k_m \delta / D^{eff}$) estimated from realistic simulations.

5.4 Model Calibration

In this section, the procedure used for calibrating the model parameters is summarized. A trial and error method was utilized for calibration. However, the procedure is not trivial and does not depend on pure luck; on the contrary, educated guesses were made by making use of a priori investigations on the effect of each model parameter on the interface contaminant coverage and thus the performance degradation.

In an attempt to determine the effect of model parameters such as effective diffusivity of the contaminant, D_X^{eff} , and the forward rate constant for the contaminant adsorption reaction, $k_{f,X}$, on performance degradation, a parametric study is conducted. In the present study, electrolyte supported cells with anode thickness of approximately 30 μm were considered since they provide more rapid results due to smaller nickel inventory. The assumed anode electrode is made of a 56 % porosity cermet with a reasonable tortuosity of 3.6.

A base case was selected using the model parameters listed in Table 5.1. A hypothetical contaminant X with 10 ppm concentration in a simulated coal syngas containing 23% CO, 30% H₂, 21% CO₂ and 26% H₂O is used. All simulations were done at atmospheric pressure. For the comparison purposes a dimensionless group, namely Thiele modulus, was utilized. This number is defined as the ratio of reaction and diffusion timescales and given as

$$\Pi = \frac{(1/k_{f,X})}{(\delta^2/D_X^{eff})} = \frac{D_X^{eff}}{\delta^2 k_{f,X}} \quad (5.22)$$

where δ is the anode thickness, $k_{f,X}$ is the forward reaction rate constant for impurity adsorption reaction and D_X^{eff} is the effective diffusivity of the impurity species. The combined effect of contaminant effective diffusivity and forward reaction rate constant was investigated using this dimensionless number. The reason for selecting a

dimensionless group is that decreasing effective diffusivity instead of increasing forward rate constant is numerically less cumbersome since increased forward rate constants results in bigger source terms for the governing equation (Eq.(5.4)) making it stiffer. Smaller time steps were required in order to solve that equation. On the other hand, decreasing effective diffusivity does not affect the time step utilized and the end results are the same as long as the Thiele modulus is kept constant.

Table 5. 1: Parameters used for the parametric analysis

Parameter	Value
Temperature, °C	800
Current density, A/cm ²	0.5
D_X^{eff} , m ² /s	1×10^{-6}
$k_{f,X}$, s ⁻¹	0.5
m	0.4
n	7.0
p	2.0
q	2.0

The effect of increasing Thiele modulus by 2.5 times or reducing it by 0.5 times on the interface coverage and the performance degradation due to the hypothetical contaminant *X* are shown in Figure 5.3 and 5.4, respectively. As can be seen from Figure 5.3, increasing the dimensionless number (by 2.5 times) decreases the time for the front to reach the active interface. In other words, increasing the contaminant effective diffusivity or decreasing the forward reaction rate constant speeds up the starting of contaminant coverage at the interface. It is also worth mentioning that, once the front reaches the active interface, the time evolution is very similar for each case. Comparing Figure 5.3 and 5.4 reveals that, since time evolution of the interface coverage is the same after the active interface is reached, the form of the performance curves are the same. The only

difference is the cell failure time which increases with the decreasing Thiele modulus. It is also observed that, there is a linear relationship between the values of the Thiele modulus and the cell failure time, i.e., decreasing Thiele modulus in half, doubles the cell failure time.

Figure 5. 3: Effect of Thiele modulus on the interface coverage for the impurity X.

Figure 5. 4: Effect of Thiele modulus on the modified power density for the impurity X.

Figures 5.5 and 5.6 show the effect of Thiele modulus on the anode surface concentration and the flux of impurity X, respectively. From Figure 5.5, it is seen that the time to reach the free stream impurity concentration decreases with increasing Thiele modulus. Once the surface concentration reaches the free stream value, the flux at the anode/fuel channel interface becomes zero, as can be seen from Figure 5.6.

Figure 5. 5: Effect of Thiele modulus on the anode surface concentration of impurity X

Figure 5. 6: Effect of Thiele modulus on the impurity flux at the anode/fuel channel interface

In addition, a sensitivity analysis was performed to determine the effect of powers m and n appearing in Eq. (5.15). These parameters control the dependence of the exchange current density for H_2 on the interface impurity coverage and thus the behavior of performance degradation. Figures 5.7 (a) and 5.7 (b) show the variation of performance degradation curve with the powers m and n , respectively. The base case calculations were carried out using the parameters tabulated in Table 5.1.

It can be seen from Figure 5.7 (a) that as the value of power m is increased all four stages of the typical performance degradation become evident. In addition, decreasing the power m leads to faster degradation of the cell without observing the third stage of the performance degradation. Similarly, increasing power n , leads to a performance curve

with all four stages of degradation with slightly higher initial degradation (see Figure 5.7 (b)).

(a)

(b)

Figure 5. 7: Variation of performance degradation with model parameters (a) m , (b) n

Making use of these observations discussed, the calibration for AsH₃, PH₃, H₂S and H₂Se were done by minimizing the difference between the performance degradation curves obtained from the current model and the experimental results for electrolyte-supported cells. Initial task in calibration process is to match the timescale for the front to reach the active interface. This time scale is adjusted by changing the effective diffusivity, keeping in mind that increasing it results in smaller time to reach the active interface and hence faster initial degradation (see Figure 5.3 for higher Thiele modulus). Second fast degradation and the final slow degradation stages in the performance degradation curve is governed by the powers m and n appearing in the exchange current density relation given in Eq. (5.15). These parameters are adjusted according to the sensitivity analysis described above. The model parameters p and q in equations (5.9) and (5.17) are increased to catch the initial fast drop in performance typically observed for H₂S. For other impurity species, their values are the same and taken as 2.0.

5.5 Results and Discussion

5.5.1 Arsine

Calibration for 10 ppm AsH₃ in a simulated coal syngas containing 23% CO, 30% H₂, 21%CO₂ and 26% H₂O was done by minimizing the difference between the performance curves obtained from the current model and the experimental results from Coyle et al. [22] and the result is given in Figure 5.8. Experiments were conducted at 800°C with a constant current density of 0.05 A/cm².

Figure 5. 8: Calibration of modified power density against experimental data adopted from Coyle *et al.* [22] for 10 ppm AsH₃ in coal syngas at 800 °C

It is seen from the Figure 5.8, it is possible to obtain a good agreement between the experimental data and the model results. The calibrated parameters are listed in Table 5.2.

Table 5. 2: Calibrated parameters for AsH₃ impurity

Parameter	Value
$k_{f,X}, s^{-1}$	$5.0 \times 10^3 \exp(-5.97/RT)$
$k_{b,X}, s^{-1}$	$9.1 \times 10^{-1} \exp(-9.27 \times 10^4/RT)$
m	0.3
n	6.5
p	2.0
q	2.0

Figures 5.9 and 5.10 show the interface coverage and the time evolution of the coverage inside the anode for arsine, respectively. It should be noted that the fourth stage of performance degradation was not observed here (see Fig 5.8) since once the contaminant coverage reaches a certain value at the interface the cell dies without stabilizing the performance. It can be seen from Figure 5.10 shows that there exists a distinct region between the covered and yet to be covered parts of the anode at different times of the simulation.

Figure 5. 9: Time evolution of the interface coverage for AsH_3 impurity

Figure 5. 10: Coverage profile for AsH_3 at different times

The space maps of porosity and electrical conductivity along with the exchange current density at different times was also shown in Figures 5.11, 5.12 and 5.13, respectively. It is clearly seen from the figures that as the available nickel sites available for H_2 adsorption are covered by the impurity over time, the porosity and electrical conductivity decreases as well as the exchange current density at the active anode/electrolyte interface. Therefore, according to the developed model, the performance degradation is due to a combined effect of reduced porosity and electrical conductivity and the deactivated electrochemical reactions due to impurity adsorption on the nickel catalyst.

Figure 5.11: Porosity profile at different times

Figure 5.12: Electrical conductivity profile at different times

Figure 5. 13: Time evolution of the exchange current density for AsH₃ impurity

Before further progression, the assumption of neglecting the losses from the cathode side is justified by including them into the simulations and comparing the results from including and omitting cathode losses. The details of cathodic overpotential calculations are given in Appendix B. The comparison results obtained for 10 ppm AsH₃ at 800 °C are given in Figure 5.14. As can be seen from the figure, although there is slight difference in the modified power density predictions, the error is so small that the cathode losses can be safely omitted from the calculations.

Figure 5. 14: Effect of including cathode losses to performance degradation calculations for 10 ppm AsH_3 at 800 °C

For better visualization of the front moving toward the active interface, the penetration thicknesses calculated from the model predictions were mapped onto a 2D plane representing the anode (Figure 5.15). As can be seen from the figure, the penetration thicknesses increase with increasing impurity concentration at a given time as well as increasing with time for a given concentration. This progression of the sharp interface with increasing contaminant concentration is strikingly similar to experimental observation as depicted in Figure 5.1.

The calibrated model is then validated using a different set of experimental data to test the ability of the model to predict the effects of impurity concentration and the operating temperature. Figures 5.16 a & b display the predicted results for concentration and temperature effects, respectively. It is seen from the figures that the calibrated model

successfully predicts the performance degradation at different contaminant concentrations and operating temperatures. It can also be seen from the figures that, although the error for P^* can be as high as 30 %, the cell failure time, which is the primary concern of this study, can be predicted with 4 h of difference.

(a)

(b)

Figure 5. 15: Penetration thicknesses at 800 °C (a) for 10 ppm AsH₃ in coal syngas after 2 h, 4 h, 6 h and 8 h of operation (b) after 10 h with 1, 5 and 10 ppm AsH₃ in coal syngas

(a)

(b)

Figure 5. 16: Validation of the calibrated arsine degradation model for (a) concentration effect (b) temperature effect

It is worth noting that all the simulations were performed at a constant current to ensure the identical conditions with the experimental data used for comparison purposes. In an attempt to identify the difference brought about by keeping the voltage constant, a simulation was done using the same conditions described above for 10 ppm AsH₃ at 800 °C at a constant voltage of 0.7 V. The boundary condition at the anode/electrolyte interface was adjusted such that the molar fluxes at that interface change proportional to the changing cell current. Figure 5.17 displays the comparison between the modified power density predictions obtained from the two approaches: keeping the cell current constant at 0.05 A/cm² and keeping the voltage constant at 0.7 V. As can be seen from the figure, the two approaches start to differ towards the cell failure time.

Figure 5. 17: Comparison between the modified power density predictions obtained by keeping the current constant at 0.05 A/cm² and keeping the current constant at 0.7 V

5.5.2 Phosphine

A similar calibrating procedure was employed for PH_3 impurity. The comparison is done with the experimental performance loss due to 5 ppm PH_3 in a simulated coal syngas containing 23% CO , 30% H_2 , 21% CO_2 and 26% H_2O at 800°C with a constant current density of 0.1 A/cm^2 [23] and the result is given in Figure 5.18.

Figure 5. 18: Calibration of modified power density against experimental data adopted from Marina *et al.* [23] for 5 ppm PH_3 in coal syngas at 800°C

In this case as well it was possible to achieve a fairly good agreement between the modified power density profiles obtained from the proposed model and the experimental data from literature. The calibrated parameters are given in Table 5.3.

Table 5. 3: Calibrated parameters for PH₃ impurity

Parameter	Value
$k_{f,X}, \text{ s}^{-1}$	5.0×10^2
$k_{b,X}, \text{ s}^{-1}$	$9.1 \times 10^{-3} \exp(-9.23 \times 10^4 / RT)$
m	0.01
n	2.2
p	2.0
q	2.0

It should be noted that the forward reaction rate constant for contaminant coverage is not a function of temperature. The reason for this is that experimental data available for electrolyte-supported cells [23] showed no clear dependence on temperature as opposed to other experiments performed on anode-supported cells [79].

The interface coverage as a function of time is given in Figure 5.19. It is evident from the comparisons of the Figures 5.18 and 5.19 that, once the contaminant coverage reaches a certain limit at the active interface, the cell fails immediately without experiencing the typical final slow degradation stage.

Figure 5. 19: Time evolution of the interface coverage for PH₃ impurity

The validation of the calibrated model was done against the experimental data to test the ability of the calibrated model to predict the effects of impurity concentration and the operating temperature. The comparison between the modified power density results obtained from the current model and those of the experiments for different impurity concentrations is shown in Figure 5.20. It is clearly seen from the figure that the model closely emulates the typical degradation patterns observed at different impurity concentrations.

Figure 5. 20: Validation of the calibrated phosphine degradation model for concentration effect

5.5.3 Hydrogen Sulfide

Figure 5.21 and 5.22 show the calibrated model results for the performance degradation due to 20 ppm H_2S in wet H_2 gas (95% H_2 /5% H_2O) and the corresponding interface coverage for the impurity, respectively. The calibration was done using experimental data of Xu [84] performed at 800 °C and a constant current density of 0.2 A/cm² and the calibrated parameters are given in Table 5.4.

Figures 5.21 and 5.22 reveal that the degradation occurs in four stages: an initial loss of activity followed by a plateau and then a period of more rapid power loss and finally a very slow degradation. As shown in Figure 5.21 the model results closely follows the experimental data except that experimental performance curve stabilizes at a higher power than the model results. Although there is a 50% difference between the predicted

results and the experimental data in that region, the results are still encouraging given the simplicity of the model.

Figure 5. 21: Calibration of modified power density against experimental data adopted from Xu [84] for 20 ppm H_2S in wet H_2 at 800 °C

Figure 5. 22: Time evolution of the interface coverage for H_2S impurity

Table 5. 4: Calibrated parameters for H₂S impurity

Parameter	Value
$k_{f,X}, \text{ s}^{-1}$	1.0×10^3
$k_{b,X}, \text{ s}^{-1}$	$1.8 \times 10^{-2} \exp(-9.28 \times 10^4 / RT)$
m	0.04
n	1.2
p	3.0
q	3.0

5.5.4 Hydrogen Selenide

Calibration for 1.5 ppm H₂Se in a simulated coal syngas containing 23% CO, 30% H₂, 21%CO₂ and 26% H₂O was also done against the experiments conducted at 700°C with a constant current density of 0.25 A/cm² [21]. Calibration result is given in Figure 5.23 along with the validation of the calibrated data for a different concentration.

As can be seen from Figure 5.23, model can successfully predict the performance degradation curve. The calibrated parameters are given in Table 5.5.

Table 5. 5: Calibrated parameters for H₂Se impurity

Parameter	Value
$k_{f,X}, \text{ s}^{-1}$	2.0×10^3
$k_{b,X}, \text{ s}^{-1}$	$9.1 \times 10^{-2} \exp(-9.25 \times 10^4 / RT)$
m	0.02
n	1.4
p	2.0
q	2.0

The interface coverage as a function of time given in Figure 5.24 shows that, the trend is similar to that of H₂S where the performance stabilizes in the final phase of the degradation.

Figure 5. 23: Calibration of modified power density against experimental data adopted from Marina *et al.* [21] for 1.5 ppm H₂Se in coal syngas at 800 °C

Figure 5. 24: Time evolution of the interface coverage for 1.5 ppm H₂Se impurity

5.6 Multi-Component Impurity

In order to account for the effect of each additional contaminant, Y , in a system of multiple impurities, an additional adsorption reaction is included in the model along with the mechanism given in Eq.s (5.2) and (5.3):

Also, Eq. (5.4) has to be solved for each additional impurity. Once the coverage profiles are obtained for the impurities in the mixture, several averaging approaches were tested for calculation of the exchange current density as a function of interface impurity coverages. First approach is the simple multiplication of the contributions from each contaminant:

$$i_{o,H_2} = i_{o,ref} \left(1 - \theta_{Ni-X,int}^m\right)^n \left(1 - \theta_{Ni-Y,int}^k\right)^l \quad (5.23)$$

where $\theta_{Ni-X,int}$ and $\theta_{Ni-Y,int}$ are the interface coverages for the impurity species X and Y , respectively. $i_{o,ref}$ is the reference exchange current density at zero percent coverage given by

$$i_{o,ref} = c_1 \left(\frac{y_{H_2,int}}{y_{H_2,ref}} \right) \exp \left(- \frac{E_{act,H_2}}{R_u T} \right) \quad (5.24)$$

Second approach evaluated is based on taking the weighted averages of the contaminant coverages at the active interface and is represented by the following closed form relation:

$$i_{o,H_2} = i_{o,ref} \left[\frac{\left(1 - \theta_{int,Ni-X}^m\right)^n \theta_{int,Ni-X} + \left(1 - \theta_{int,Ni-Y}^k\right)^l \theta_{int,Ni-Y}}{\theta_{int,Ni-X} + \theta_{int,Ni-Y}} \right] \quad (5.25)$$

In the third approach, the exchange current density is assumed to be a function of harmonic averages of the interface coverages of the impurities:

$$i_{o,H_2} = i_{o,ref} \left[\frac{(\theta_{int,Ni-X} + \theta_{int,Ni-Y}) \left(1 - \theta_{int,Ni-X}^m\right)^n \left(1 - \theta_{int,Ni-Y}^k\right)^l}{\theta_{int,Ni-X} \left(1 - \theta_{int,Ni-Y}^k\right)^l + \theta_{int,Ni-Y} \left(1 - \theta_{int,Ni-X}^m\right)^n} \right] \quad (5.26)$$

Another approach is to use the weighted average of the powers. As the name implies, the interface coverage dependence of the exchange current density is represented by the weighted averages of the powers, m , n , k and l and given by the following equations:

$$m^* = \frac{m\theta_{\text{int},Ni-X} + k\theta_{\text{int},Ni-Y}}{\theta_{\text{int},Ni-X} + \theta_{\text{int},Ni-Y}} \quad (5.27a)$$

$$n^* = \frac{n\theta_{\text{int},Ni-X} + l\theta_{\text{int},Ni-Y}}{\theta_{\text{int},Ni-X} + \theta_{\text{int},Ni-Y}} \quad (5.27b)$$

$$\theta_{\text{int}}^* = \theta_{\text{int},Ni-X} + \theta_{\text{int},Ni-Y} \quad (5.27c)$$

$$i_{o,H_2} = i_{o,ref} \left(1 - (\theta_{\text{int}}^*)^m \right)^n \quad (5.27d)$$

In what follows, the approaches explained above were applied to multi-component impurity cases including AsH₃ and PH₃; AsH₃ and H₂S; PH₃ and H₂S; AsH₃, PH₃ and H₂S. The model predictions were not compared to any experimental data since there are only a few studies in the literature considering the synergistic effects of the coal syngas impurities and these experiments are performed on anode-supported cells [17, 81].

All the simulations are performed for an electrolyte supported cell with an anode thickness of 30 μm and at a typical SOFC operating temperature of 800 °C. Current density is kept constant at 0.1 A/cm² for all simulations. The coal syngas composition is 23% CO, 30% H₂, 21%CO₂ and 26% H₂O.

5.6.1 Arsine and Phosphine Mixture

The synergistic effect of 5 ppm AsH₃ and 5 ppm PH₃ on the cell performance was tested using the averaging techniques described above for effective exchange current density as a function of the interface coverages and the results are given in Figure 5.25. As can be seen from the figure, adsorption reaction kinetics for arsine is much faster than that of phosphine and thus, modified power density results from all the averaging techniques collapse down to arsine degradation curve with slightly less performance than single AsH₃ impurity case.

Figure 5. 25: Comparison of performance loss for a mixture of 5 ppm AsH_3 and 5 ppm PH_3 with different averaging techniques

The result of fast kinetics of arsine coverage is clearly seen in Figures 5.26 and 5.27 which show the change in interface coverages with time and the concentration profiles along the thickness of the anode after 20 hours, respectively. Figure 5.26 illustrates that, the interface coverage for arsine reaches its highest value when the front of phosphine coverage just arrives at the active interface. In addition, arsine concentration reaches the prescribed free stream concentration long before phosphine impurity (see Figure 5.27). Since the apparent concentration for AsH_3 inside the anode is approximately five times more than that of PH_3 , mixture performance curve follows the AsH_3 degradation path.

Figure 5. 26: Time evolution of interface coverages for 5 ppm AsH₃ and 5 ppm PH₃

Figure 5. 27: Concentration profiles for 5 ppm AsH₃ and 5 ppm PH₃ along the thickness of the anode at t = 20 h

5.6.2. Arsine and Hydrogen Sulfide Mixture

The performance degradation due to 5 ppm AsH₃ and 5 ppm H₂S was also tested and results with different averaging techniques are given in Figure 5.28. Investigation of figure reveals that, replacing 5 ppm PH₃ for 5 ppm H₂S does not change the performance results regardless of the averaging technique used.

Figure 5. 28: Comparison of performance loss for a mixture of 5 ppm AsH_3 and 5 ppm H_2S with different averaging techniques

Interface coverages as a function of time for AsH_3 and H_2S impurities is given in Figure 5.29. Similar to AsH_3 and PH_3 mixture case, interface coverage for AsH_3 is about nine times more than that of H_2S meaning all 90% of all the available catalyst sites are covered by AsH_3 impurity and only 10% is covered by H_2S and H_2 . Moreover, it is shown in Figure 5.30 that, the concentration of AsH_3 at the active interface is five times more than that of H_2S .

Figure 5. 29: Time evolution of interface coverages for 5 ppm AsH_3 and 5 ppm H_2S

Figure 5. 30: Concentration profiles for 5 ppm AsH_3 and 5 ppm H_2S along the thickness of the anode at $t = 20$ h

5.6.3 Phosphine and Hydrogen Sulfide Mixture

Next analysis investigates the effect of multi-component impurity including 5 ppm PH_3 and 5 ppm H_2S . Results obtained with different averaging techniques are given in Figure 5.31. As can be seen from the figure, mixture of impurities leads to lower cell performance than that of the lowest of two single impurity cases for all the averaging techniques utilized. In addition, when multiplication and weighted powers averaging methods were used the cell fails at around 60 hours whereas weighted average and harmonic average methods lead to a low value of stable power around that time of operation.

Figure 5. 31: Comparison of performance loss for a mixture of 5 ppm PH_3 and 5 ppm H_2S with different averaging techniques

Figure 5. 32: Time evolution of interface coverages for 5 ppm PH₃ and 5 ppm H₂S

Figure 5.32 displays the time evolution of interface coverages for the phosphine and hydrogen sulfide impurities. As can be seen from the figure, the interface coverages reach their maximum possible values at around time = 60 h. This time should be the time when the degradation curve either stabilizes at a lower value or fails. However, it was shown in the experiments performed for anode-supported cells that the performance does not exhibit a stabilized performance but it continues to degrade at a constant rate [17]. Therefore, degradation curves obtained by using multiplication or weighted powers techniques are more realistic compared to weighted average and harmonic average methods. Figure 5.32 also shows that the values of the interface coverages for both impurity species are similar with phosphine interface coverage being slightly higher. Concentration profiles along the thickness of the anode also show that the phosphine concentration is slightly higher. (see Figure 5.33)

Figure 5. 33: Concentration profiles for 5 ppm PH_3 and 5 ppm H_2S along the thickness of the anode at $t = 50$ h

5.6.4 Arsine Phosphine and Hydrogen Sulfide Mixture

Finally, the synergistic effect of a mixture of three impurities including 5ppm PH_3 , 5 ppm H_2S and 5 ppm AsH_3 in a simulated syngas was investigated using the multiplication averaging technique and the result is given in Figure 5.34.

Figure 5. 34: Performance degradation for a mixture of 5 ppm AsH_3 , 5 ppm PH_3 and 5 ppm H_2S

It can be seen from the figure that addition of 5 ppm phosphine on top 5 ppm hydrogen sulfide results in a sudden initial performance loss of 40%, however, the rate of degradation is rather slower for the next 20 h of operation. When 5 ppm arsine is also added to the fuel, cell degrades rapidly and completely fails within 5 hours.

5.7 Estimation of Tolerance Limits

The ultimate goal of this study is to establish the minimum allowable impurity concentrations in coal syngas intended to be used in SOFCs operating for over 10,000 h. Arsine and phosphine are the two impurities that are known to have the most deleterious effects of the cell performance due to their affinity to have strong relations with the anode catalyst by formation of secondary phases. Numerically determined lifetimes of the cells can provide a basis for estimation of SOFC stack lifetimes operating on coal syngas.

Extrapolation of accelerated results at relatively higher concentrations can provide guidance into predicting the cell failure at low impurity concentration.

A summary of cell lifetimes for electrolyte-supported cells with an anode thickness of 30 μm operated in simulated coal syngas containing 23% CO , 30% H_2 , 21% CO_2 and 26% H_2O and varying concentrations of AsH_3 impurity is given in Figure 5.35. The criterion for cell failure is taken as the time when 60 % of power loss occurs.

Figure 5. 35: Time to cell failure for electrolyte-supported cells exposed to simulated coal syngas with varying concentrations of arsine at different operating temperatures

As can be seen from the figure, a power law type of curve was fit to the numerical results at different temperatures. Extrapolation of the fitted curve to lower impurity concentrations shows that for 10,000 h of operation, the minimum allowable impurity

concentration is estimated to be about 5 ppb. The closed form relation extracted from the numerical results for estimating the lifetime of electrolyte-supported cell can be given by:

$$t_{\text{failure}} = 1.19 \times 10^6 \left(\frac{C}{C_{\text{ref}}} \right)^{-0.87} \left[1 - 3.48 \times 10^{-4} \left(\frac{T}{T_{\text{ref}}} \right) \right] \quad (5.23)$$

where C is the impurity concentration in ppm, T is the operating temperature in °C . Reference concentration, C_{ref} , and reference temperature T_{ref} are taken as 0.5 ppm and 700 °C, respectively.

In an attempt to include the anode thickness into the prediction of cell failure time more simulations were run for 10 ppm AsH₃ in coal syngas at 800 °C the results are given in Figure 5.36. As it is seen from the figure, there is a linear relationship between the cell failure time and the anode thickness.

Figure 5. 36: Time to cell cells exposed to simulated coal syngas with 10 ppm of AsH₃ coal syngas at 800 °C with varying anode thicknesses

Similar analysis was done for phosphine using the same composition for the coal syngas. Figure 5.37 summarizes the cell failure times at different concentration of PH_3 . Since experiments show no dependence of cell performance on temperature for electrolyte-supported cells, the analysis was done at one temperature of 800 °C.

Figure 5. 37: Time to cell failure for electrolyte-supported cells exposed to simulated coal syngas with varying concentrations of phosphine at 800 °C

As can be seen from the figure, extrapolation of the power law type of curve fit to lower impurity concentrations shows that for 10,000 h of operation, the minimum allowable impurity concentration is estimated to be about 0.2 ppb. The closed form relation extracted from the numerical results for estimating the lifetime of electrolyte-supported cell can be given by:

$$t_{\text{failure}} = 7.15 \times 10^2 \left(\frac{C}{C_{\text{ref}}} \right)^{-0.83} \quad (5.24)$$

Here again the cell failure time, t_{failure} , was assumed to occur when 60 % of the power is lost.

CHAPTER 6- CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

- A new phenomenological model is formulated to predict the typical degradation patterns observed in SOFC anodes due to coal syngas impurities.
- Model parameters such as reaction rate constants for the adsorption reactions are obtained through indirect calibration to match the degradation rates reported in the literature for Arsine (AsH_3), Phosphine (PH_3), Hydrogen Sulfide (H_2S) under accelerated testing conditions
- Parametric studies performed at different impurity concentrations, operating temperatures and current densities showed that the coverage rate increases with increasing temperature and impurity concentration as expected.
- Calibrated model was then used for prediction of the performance curves at different impurity concentrations and operating temperatures. Encouraging agreement was obtained between the predicted results and the experimental data reported in the literature.

- Synergistic effect of various impurities including AsH_3 , PH_3 and H_2S was also examined and it was concluded that the mixture of impurities leads to faster degradation and thus shorter lifetime of the cell when compared to that of a single impurity.

6.2 Future Work

The model could be further advanced by incorporating the following aspects into it:

- The model can be extended to include the kinetics of formation of secondary phases with the anode material
- Modeling of nickel migration to the anode surface which is observed with impurity species forming secondary phases with the anode material can be incorporated
- Interactions of the impurities with LSM part of the anode which is shown to affect the performance degradation can also be included in the surface reaction mechanism
- A more advanced calibration technique can be utilized
- Model parameters to minimize the effect of experiments performed at different conditions can be included
- The developed degradation model can be included into a detailed multi-dimensional model for simulation of transport phenomena in SOFCs such as DREAM-SOFC
- A more sophisticated surface reaction mechanism for multiple impurities that allows for mutual interactions between various impurities can be incorporated.

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APPENDIX A

Effect of Using Different Numerical Time Steps on Equilibrium Concentration of Ni_5P_2

The assumption of using a numerical time step of 1 sec in the transient equilibrium calculations was justified by repeating calculations at 750 °C and 1 atm using an initial PH_3 concentration of 5 ppm and a current of 0.5 A using a numerical time step of 10 sec. It should be noted that as a numerical limitation of Cantera 1.7, any time step smaller than 1 sec was not able to be used.

Figure A.1 shows the comparison between the percentage of nickel converted to nickel phosphide results obtained by using numerical time steps of 1 sec and 10 sec. It can be seen that the results do not change when a time step of 10 s is used which means 1 s is enough for equilibrium.

Figure A 1: Effect of using a numerical time step of 10 sec on % Ni converted to Ni_5P_2

APPENDIX B

Calculation of Cathode Losses

Oxygen activation overpotential is simply calculated from Butler-Volmer equation with the assumption that the transfer coefficient α is 0.5

$$\eta_{act,O_2} = \frac{R_u T}{2\alpha F} \sinh^{-1} \left(\frac{i_{O_2}}{2i_{o,O_2}} \right) \quad (B.1)$$

where i_{O_2} is the current density. Oxygen exchange current density is given by

$$i_{o,O_2} = \frac{c_3}{(T - 279.1757)^{1/2}} \left(\frac{y_{O_2,int}}{y_{O_2,ref}} \right) \exp \left(-\frac{E_{act,O_2}}{R_u T} \right) \quad (B.2)$$

where the reference oxygen concentration, $y_{O_2,ref}$, is 0.21, the activation energy barrier, E_{act,O_2} , is 120 kJ/mol, and the constant c_3 is 5.874×10^9 [83].